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THE UNIVERSITY OF ALBERTA

AN APPROACH TO GENESIS OF PINE POINT MINERALIZATION, N.W.T. CANADA

by

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A thesis submitted to the Faculty of Graduate Studies in Partial Fulfilment of
the Requirements for the Degree of Master of Science.

Department of Geology

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UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled, "An Approach to Genesis of Pine Point Mineralization, N.W.T., Canada", submitted by R.N. Singh, M.Sc., in partial fulfilment of the requirements for the degree of Master of Science.

ABSTRACT

In the Pine Point Orefield, lead-zinc deposits occur in Middle Devonian dolomite. Experimental studies by the writer include the determination of FeS contents in ZnS, MgCO_3 in calcite lattice, minor elements in sulfides, textural relationship and isotopic variation. Nine samples of dark and light sphalerite were examined by chemical and X-ray methods to determine temperature range. Results indicated a lower limit of 1 mole % and an upper limit of 15.8 mole % FeS in ZnS. The average temperature of mineralization suggested by this study was less than 260°C . The presence of Se, Sb, Cd, Cu, Sn, Bi, Mn, Ga, Ge and In as minor elements in addition to Fe, Zn, and Pb as major elements was determined by X-ray fluorescence study of twenty-eight samples. Experiments performed on seventeen calcite samples to determine Mg content present as MgCO_3 in solid solution in CaCO_3 by X-ray diffraction method indicate either no or a negligible shift in calcite peaks which in turn indicate no replacement of Ca by Mg in calcite lattice. This is a further indication of low formation temperature for Pine Point carbonates.

Thirty polished and thin ore sections were examined in detail for textural interpretation. This study afforded an explanation for the replacement and cavity filling nature of these deposits and also suggested a probable paragenetic relationship. An effort was made to make use of oxygen isotopes in predicting paleotemperatures for carbonates and associated mineralization. This latter study indicates a range of $50^\circ - 100^\circ\text{C}$ for Pine Point mineralization.

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CHAPTER - I

INTRODUCTIONGENERAL STATEMENT

In 1965 two outstanding events took place in the mineral industry of the Northwest Territories. Firstly a substantial increase in the value of mineral production and secondly the Pine Point staking rush - similar to the rush in Klondike days. Both of them have strengthened the economy of the nation. Today, Pine Point ores are a matter of great interest from the viewpoint of their academic and economic standing.

Pine Point mineralization is of unusual type as indicated by the experimental studies. The theme of this thesis has been to gather clues regarding a plausible explanation for the genesis of sulfide mineralization at Pine Point. Bearing in mind the significance of the present problem the experimental studies were performed from the viewpoint of the textural, geochemical and isotopic interpretation of sulfide ores, with the main emphasis laid on the textural and isotopic interpretation. The isotopic investigation in the present case is mostly concerned with oxygen and carbon isotope studies used to interpret the palaeotemperature of carbonates from Pine Point⁺. Since the development of the carbonate palaeotemperature scale by Urey and his associates (1951) the application of this study has been extended to problems of igneous and metamorphic rocks and hydrothermal mineral deposits. Recent years have seen advances in this field and the best possible efforts were made to make use of available information to interpret the nature and conditions of mineralization.

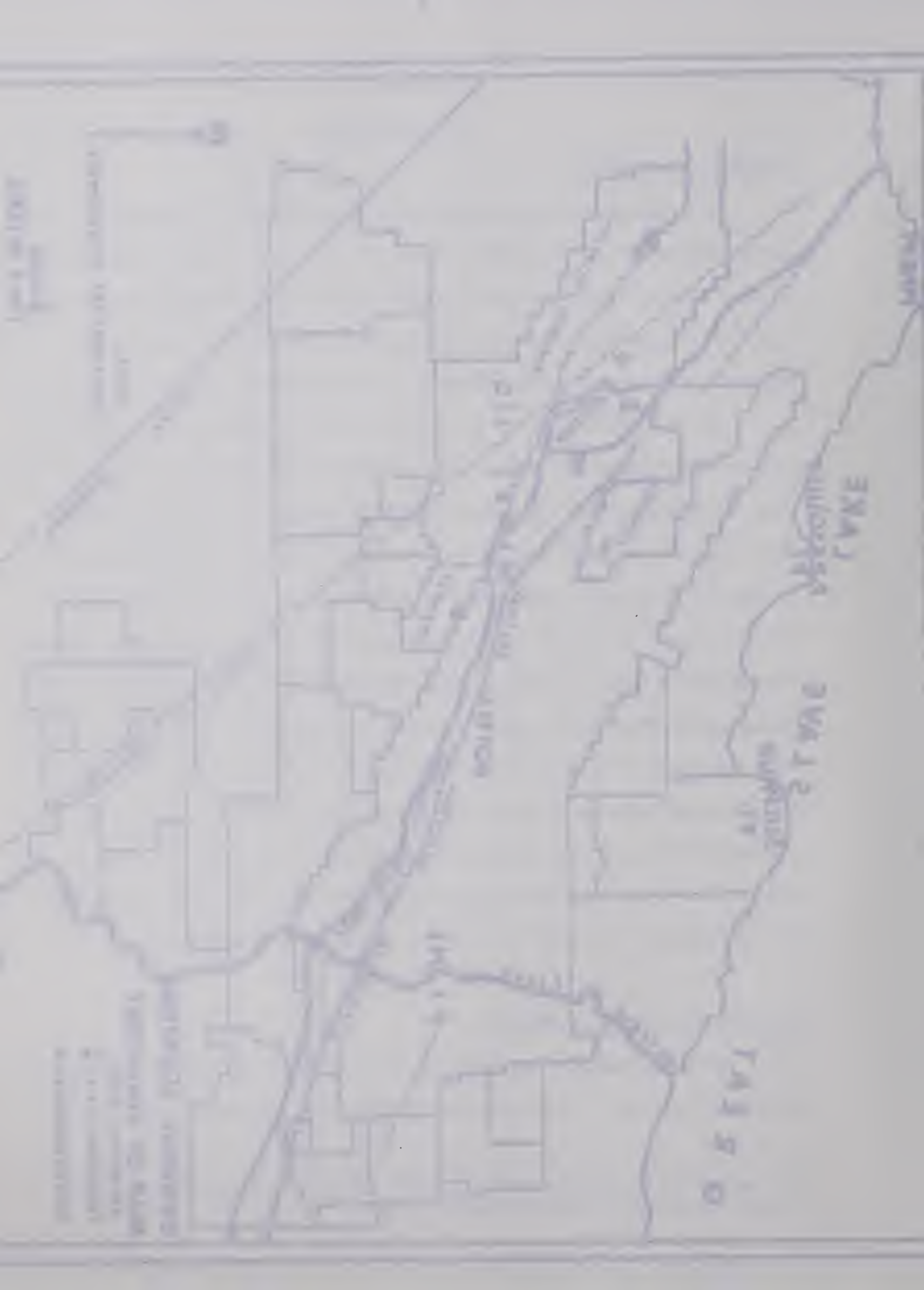
LOCATION AND ACCESSIBILITY

The Pine Point area is situated near the south shore of Great Slave Lake in the Northwest Territories. The area of active exploration lies between 60° and 62° N

⁺The term "Pine Point Carbonates" is used for Presqu'île carbonates throughout this thesis unless otherwise mentioned specifically.

FIG. 1

RS.



latitude and 112° to 116° W longitude. The open pits at Pine Point are located approximately $60^{\circ} 51'$ North latitude and $114^{\circ} 22'$ West longitude, about 510 air miles north of the city of Edmonton, Alberta. The Pyramid pits are located 10 miles NE of the Pine Point townsite and about 30 miles SW of the Precambrian Shield (Figures 1 & 2).

The main trading center for the activity in the area is Hay River, N.W.T., providing regular air and road services. Recently a new airstrip was built about 3 miles from Pine Point townsite. The construction of the Great Slave Lake Railway with a branch line to Pine Point was completed at the cost of 86 million dollars in 1964. This has provided a prime facility for regular shipments of concentrates and supplies, and extensions from the Grimshaw highway provides an all weather road access to Pine Point.

Topographically, the Pine Point area is one of low relief and poor drainage, characterized by open swampy muskegs, shallow ponds and glacial drift cover, but a series of gravelly raised branches provide a well drained townsite at Pine Point and materials for the access roads.

HISTORICAL BACKGROUND

Pine Point lead-zinc deposits were known to local Indians as early as 1897, and they tried to tell of this to fur traders and prospectors proceeding on to participate in the Yukon gold rush. In 1898 a fur trader by the name of Edmund Nagle came to know about the sulfide mineralization from the same local Indians and he was the first white man known to stake claims in the Pine Point vicinity. It is noteworthy that he was also the first white man to bring this information on record by official staking of eight claims. Subsequently, his claims lapsed when it became known that Pine Point deposits did not contain any gold or silver. However, the first geological report prepared by Dr. Robert Bell, then the Director of the Geological Survey of

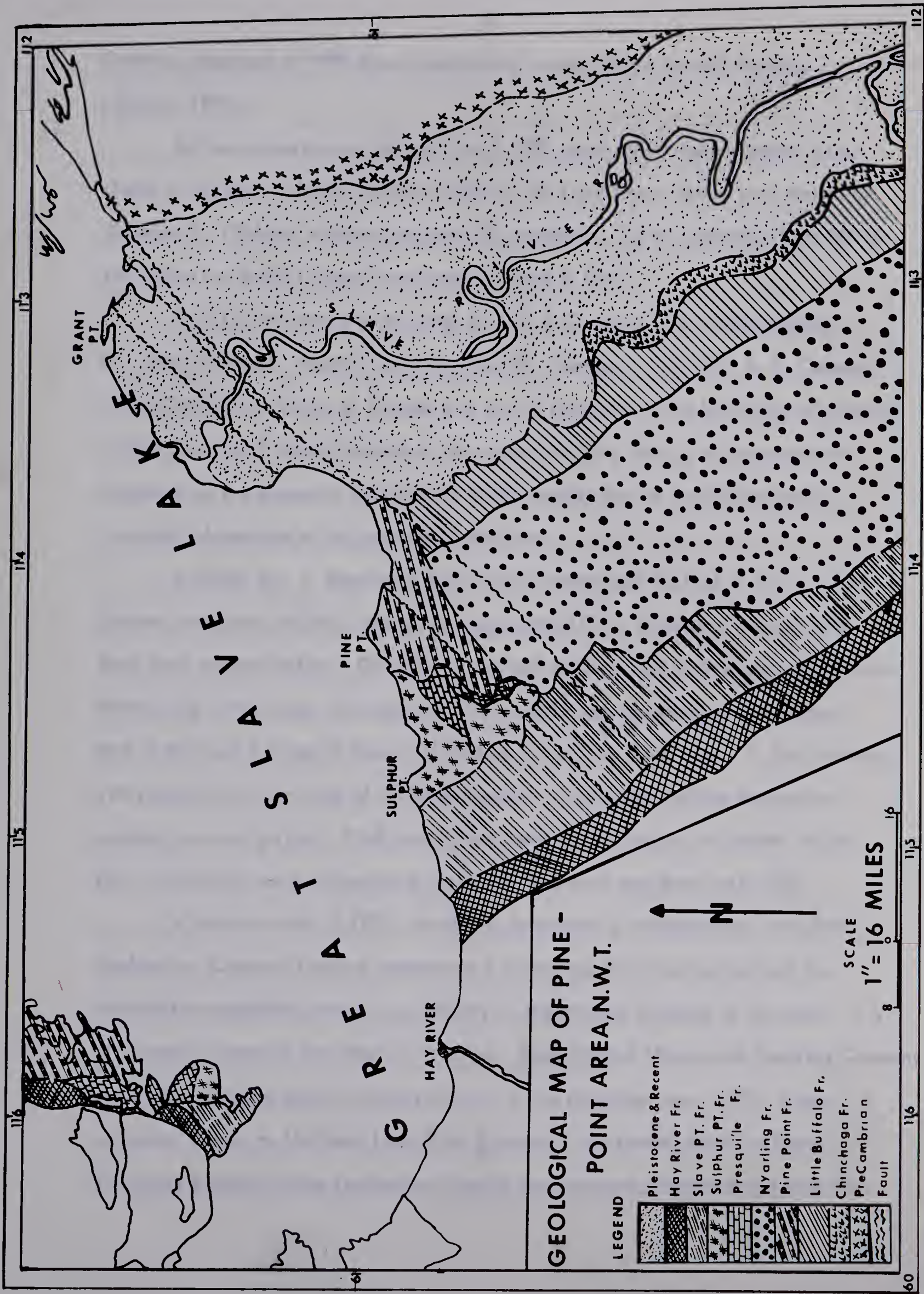


FIG. 2

(After Norris)
1965

RS

Canada, appeared in 1899 after a preliminary survey of the mineral showing, (Jordan, 1966).

Serious attention was not paid until 1908 when John Erickson staked a few claims in the area. Almost six years later in 1914 additional claims were staked by Gwynne G. Gibbins, a mining engineer by profession. In the meantime First World War broke out and all these claims were allowed to lapse.

In 1914, the area was revisited by a G.S.C. team, this time headed by Dr. Chas. Camsell. Nearly two years after Dr. Camsell's visit, Dr. A.E. Cameron of the Geological Survey of Canada and also at that time of the University of Alberta, visited the area of mineralization in the vicinity of Pine Point. He was not much impressed by the economic possibilities of the deposits but he contributed much valuable information on the geology of the area.

In 1920, Dr. J. MacIntosh Bell, who accompanied the first G.S.C. investigation team back in 1899, sent an engineer named C.B. Dawson to examine the Pine Point mineralization. Dawson was assisted and financed by the Boston Syndicate for this trip to the area. His report was favourable and subsequently in the later part of the year a group of claims was staked in the Pine Point area. In the following years under the supervision of Bell and Dawson, a systematic surface exploration program was carried out. Shaft sinking and sampling was done in a number of test pits. The results were encouraging but no further work was done until 1928.

In the later half of 1928, the Boston Syndicate in collaboration with Atlas Exploration Company Limited commenced a joint program to further explore the possibilities regarding economic suitability of the mineral showings in the area. It is of interest to mention here that by this time, Consolidated Mining and Smelting Company of Canada, Limited came into the picture. In the following year, 1929, a new company, known as Northern Lead-Zinc Company, was formed after the Boston Syndicate Limited, Atlas Exploration Limited and Ventures Limited united with the

Consolidated Mining and Smelting Company. Dr. J. MacIntosh Bell became the first managing Director of this new concern. Under his advice and supervision a detailed surface and sub-surface exploratory program began to take shape. Shafts were sunk to a maximum depth of 100 feet and numerous pits were trenched on the mineralized outcrops. The program was supported by diamond and churn drilling activities. By the end of four months, which extended from the later part of 1929 to early part of 1930, a total of 243 boreholes were completed. Of these 30 boreholes comprising 2,898 feet of diamond drilling and 213 boreholes comprising 21,601 feet of churn drilling, were drilled on the discovery showings. These efforts indicated the presence of nearly 0.5 million tons of lead-zinc "ore" in the mineral showings.

By this time all the known discovery showings were thoroughly investigated but results were not encouraging enough to support a mining operation in such remote terrain. The following years were quite inactive, until 1937 when Cominco again sank a couple of shafts and test pits to protect its interest in Northern Lead-Zinc Company Limited. No spectacular success was achieved and as a result by the end of 1940 the property at Pine Point was reduced to 104 claims. No detailed work was done till 1948 except for occasional assessment activities just to retain the claims.

In 1948, once again serious efforts were made to develop the property at Pine Point. This time Dr. Neil Campbell of Cominco was placed in charge of the Pine Point exploration program. Based on the G.S.C. information regarding Precambrian faults in the east arm of the Great Slave Lake, Dr. Campbell theorized that these faults could be extended southwesterly to Pine Point beneath the cover of Palaeozoic sediments. Considering the suitability and probable applicability of this theory, Cominco acquired a 500 square mile concession from the Department of Northern Affairs. The concession was jointly shared by Ventures Limited, Northern Lead-Zinc Company and Consolidated Mining and Smelting Company of Canada Limited. The Northern Lead-Zinc Company was offered one-third interest and

Cominco undertook the responsibility for financing and supervising the exploration activities in the Pine Point area.

An enthusiastically activated exploration program under the direct control of Cominco had come into operation in 1948 and a decision was made either to prove or disprove the further possibilities for a mining operation in the vicinity. The program was proved partially successful and indicated the presence of orebodies having no expression on the surface. As many as 42 boreholes were drilled at this time at the cost of 8,875 feet of diamond drilling. Provisions and new plans were made to develop the property.

In 1951, Pine Point Mines Limited was formed and started operations under direct control of Cominco Ltd. which has 69.12% interest in the property (Financial Post Survey of Mines, 1967). Cominco continued its exploratory program based on wide and close patterns of drilling, on and about the new mineralized belts and in 1953, two new orebodies were investigated.

By the end of 1955, the exploration program which actually commenced in 1940 had come to an end. During this time 179,936 feet of diamond drilling, 358 feet of sinking and 771 feet of other underground work had been completed in the Pine Point area. A new picture of future prospects began to appear in the vicinity of Pine Point. First estimated reserves were disclosed at this time and indicated 5,000,000 tons of combined lead-zinc ore with an average grade of 4% lead and 7% zinc (Campbell, 1966). Also the possibilities in future development of the property had been assured. In 1955, further work was terminated due to lack of adequate transportation facilities and low lead-zinc prices (Cheney, 1963).

To investigate the possibility of a suitable railway route, a three-man Royal Commission was appointed in 1959 on the adoption of the project by the Federal Government. The terms of reference of this commission were "To inquire into and report upon the respective merits of the alternative routes which might be followed by a railway line to be built from northern Alberta into the southern portion

of the District of Mackenzie, North West Territories, for the purpose of providing access to and contributing to the development of that portion of the Territories tributary to Great Slave Lake." The mutual agreement was a result of understanding between the Federal Government, Canadian National Railway Company, Cominco Limited, and Pine Point Mines Limited. By the conditions of the agreement, the Government undertook the responsibility of constructing a railway line to Great Slave Lake with a branch line to Pine Point, and Cominco undertook to place the property in production with at least 215,000 tons of concentrate shipment per year for a period of ten years (Jordan, 1966).

Pine Point Mines Limited agreed to pay normal freight rates and a little surcharge on each ton of concentrate during the period of agreement. This amount could be in the order of \$20,000,000 over the ten year period.

The Slave Lake Railway to Hay River with a spur to Pine Point was completed in 1964 at the cost of 86 million dollars. Immediately after the successful agreement for the construction of the railway line, the tempo of activities attained the highest peak. On completion of the railroad agreement, plans were considered to produce the power. With the help of Mr. Gordon Robertson, then the Deputy Minister of Northern Affairs, an agreement was made with the Northern Canada Power Commission. Thereupon N.C.P.C. built a 24,000 H.P. hydro installation on the Talston River, the cost of which is underwritten by Pine Point Mines Ltd. (Jewitt, 1966). The plant at present provides power to Pine Point and Fort Smith at reasonable cost. Exploration activities were accelerated by the adoption of new drilling appliances and by more reliable prospecting methods. The consistent utilization and investment of money, time and efforts proved a booming success for the Pine Point operation. Pine Point Mines Limited disclosed in its 1965 annual report about 21.5 million tons of combined lead-zinc ore reserves with an average grade of 4% lead and 7% zinc and in 1966; 37,800,000 tons averaging 2.9% lead and 6.8% zinc (including

Pyramid reserves). It was also reported in the Company's report of 1965 that a net profit of \$22,132,000 was earned by the shipment of ores and concentrates while in 1966 the net earnings amounted to \$34,194,000. The total shipment of concentrates and ores in 1965 valued at \$26,482,000 (Campbell, 1966).

Besides Pine Point proper mineralization, there is another noteworthy property in the vicinity. This property used to belong to Pyramid Mining Company. The reserves are in the order of 11.2 million tons of combined lead-zinc ores having an average grade of 2.5% Pb and 8% Zn (Financial Post, Survey of Mines, 1967). The interest of Pine Point Mines Limited in the Pyramid Property led to a mutual agreement and as a result of successful negotiation the sale deed was completed on the 15th day of June, 1966. Two more properties worth mentioning - Conwest and Coronet are present in the Pine Point vicinity. Conwest indicated reserves of 1,250,000 tons of 13% combined lead-zinc, while Coronet deposits are reported to be in the order of 1,100,000 tons with a grade of 13.1% combined lead-zinc (Financial Post, Survey of Mines, 1967).

PRESENT ACTIVITIES

Since the discoveries of high grade lead and zinc ore on the property of Pyramid Mines Limited in late 1965, there has been a substantial increase in staking the ground. From October 1965 to date more than 20,000 claims have been recorded in the Pine Point area. The total staked area covers approximately 20 miles long and 30 miles wide of swampy terrain. These claims have been acquired by more than 20 companies interested in exploring the possibilities for setting up mining operations. Presently many of them are either engaged or planning to start detailed prospecting by means of advanced geochemical and geophysical methods. Today, staking and mining activities are in progress even under sub-zero weather conditions where the mean temperature remains close to -25°F and sometimes reaches as low as -50°F.

The production from Pine Point proper is in consistent progress. The rated

capacity for milling ore is 5,000 tons per day which is supplied to newly built concentrator at Pine Point. The annual production of 248,000 tons of concentrates from the open pits at Pine Point is according to expectation. Serious efforts are being made to develop the property and increase the production.

CHAPTER - II

GEOLOGICAL SETTINGREGIONAL OUTLOOK

The Great Slave Lake region embraces part of the Precambrian shield in the northeast and part of the Interior plains in the southwest. This lake is the fifth largest lake on the North American continent. The east arm of the lake lies within the Precambrian shield area while the west arm is underlain by Palaeozoic and younger rock units.

A drainage system comprised of Slave River, Little Buffalo, Buffalo and Hay Rivers, those are the major streams in the Pine Point area. Numerous glacial lakes and abandoned stream channels are seen in the Slave River valley. The terrain is marshy, full of muskegs and shallow ponds. Physiographically, the Precambrian Shield is typical of the region, with bedrock exposed along the shore of Great Slave Lake and main rivers. Interior plains are low-lying, grass covered and marshy. Most of the area southwest of Great Slave Lake is low except for some higher ground which is covered with sparse vegetation (Douglas, 1959).

Structurally, Precambrian strata of eastern Great Slave Region are folded and intruded by granite, diorite and diabase (Stockwell, 1936). Several northeasterly trending faults are present in the east arm of the Great Slave Lake region which continue beneath the Palaeozoic sediments to Pine Point area (Burwash, 1957).

STRATIGRAPHIC SETTING

The Pine Point area includes ten major stratigraphic units. Detailed lithological descriptions, based on the information and interpretation of drill cores and cuttings and correlation on a regional scale, have been published by many workers in recent years (Hunt 1954, Law 1955, Campbell 1957, Douglas 1959, Belyea and Norris 1962 and Norris 1965). Devonian carbonate rocks are by far the most significant stratigraphic units as they pose a complex lithological problem and also

serve as host rock for Pine Point mineralization. The varied lithology and profound facies changes have given an extraordinarily complicated stratigraphy. The change was probably affected by shifting depositional environment throughout Middle Devonian time. These stratigraphic units were deposited on an old erosion surface that bevelled granitic intrusions and upturned the edges of older sedimentary rocks (Lord, 1951). The stratigraphic succession in the Pine Point area is represented in Table No. 1 and Fig. 3. The area of present consideration lacks Ordovician, Silurian and Lower Devonian rock units, in addition to whole Mesozoic succession. The Middle Devonian carbonate sediments directly overlie the basement complex with a distinctly demarcated unconformity. The Slave Point uppermost member of Middle Devonian is unconformably separated from Hay River member which is Upper Devonian in age. Pleistocene and Recent glacial and alluvial sands and silts cover a considerable portion of the area. A precise account of each stratigraphic Unit is represented as following:

Precambrian Unit -

The Precambrian rocks are exposed in the east arm of the Great Slave Lake (Stockwell, 1936) and in the Taltson River area (Lord, 1951). They consist mostly of diorite, granodiorite and granite. Subsurface data from Cominco's testwells G-1 and G-4 indicate that samples obtained at the depth of 1173' and 1143' exhibit orthoquartzitic and silicplutonic nature (Burwash, 1957). Recent K/Ar age determinations permit one to include Great Slave Lake basement complex in the Early Proterozoic. It seems major events took place during the period of Hudsonian orogeny which occurred some 1700-1800 m.y. ago (Burwash et. al, 1964).

Chinchaga Formation -

Law in 1955, proposed the name Chinchaga Formation for the basal unit of the Elk Point Group in the subsurface of northwestern Alberta. This unit consists of anhydrite, brown in colour, and minor amounts of cryptocrystalline dolomite. The

TABLE NO. 1

TABLE OF FORMATIONS, PINE POINT AREA, N.W.T. (After Norris, 1965)

Era	Period or Epoch	Formation or member	Lithology
Cenozoic	Pleistocene & Recent	-	Deltaic alluvial sand and silt with glacial debris, beach deposits of sand and gravel.
-U-N-C-O-N-F-O-R-M-I-T-Y-			
	Upper Devonian	Hay River	Richly fossiliferous argillaceous limestone with shale partings, medium to coarse grained dolomite.
-U-N-C-O-N-F-O-R-M-I-T-Y-			
PALAEOZOIC	MIDDLE DEVONIAN	Slave Point	Brown fine grained stromatoporoidal limestone, finely fragmental limestone with argillaceous and carbonaceous material. Amco shale marker at the base.
		Sulphur Point	Light brown, white weathered stromatoporoidal limestone, pale to dark brown argillaceous limestone, sandy limestone, medium to fine grained, dark brown dolomite.
		Presqu'ile	Massive, coarse to medium grained, vuggy dolomite, recrystallized dolomite-probably reefoidal in nature. Pb-Zn mineralization.
		Nyarling	Gypsum, minor limestone, little dolomite. Poorly exposed in southern part of Great Slave Lake.
		Pine Point	Five or more types of lithofacies, variable thickness. Fine to medium grained limestone, black bituminous shale, bluish grey limy shale, fine to coarse grained dolomite.
		Little Buffalo	Medium brown argillaceous limestone, with shale partings, gypsiferous dolomite, crinoidal limestone.
		Chinchaga	Gypsum, limestone, dolomite, limestone and dolomite breccia, salt and green shale.
-U-N-C-O-N-F-O-R-M-I-T-Y-			
Proterozoic			Granite, granodiorite and quartzdiorite.

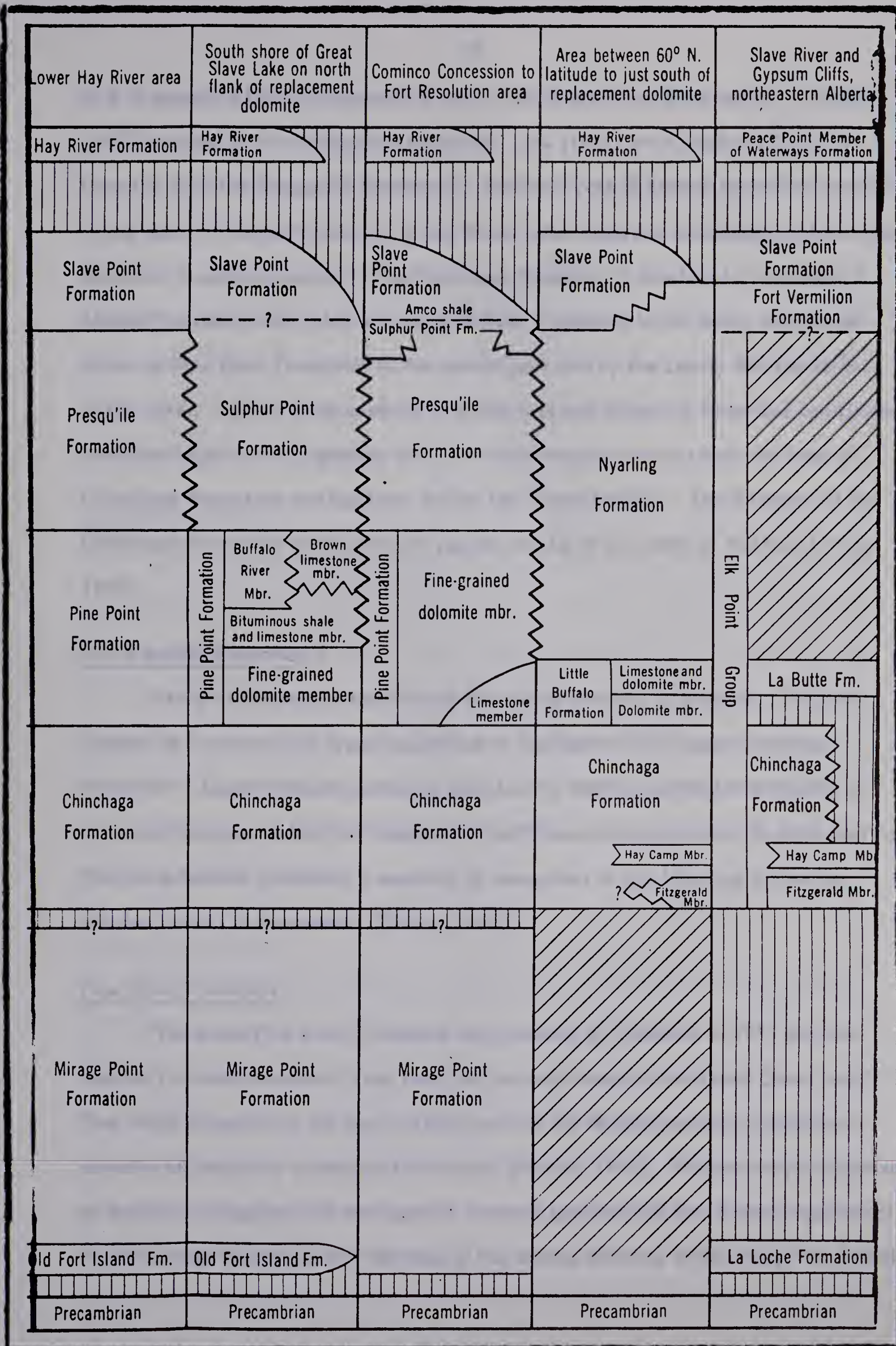


Fig.3-Nomenclature and Stratigraphic units, Pine Point Area, N. W. T. Canada .

(After Norris, 1964)

unit is traceable from northwestern Alberta into Great Slave Lake region. Cameron (1922) referred to it as Fitzgerald dolomite. Law (1955) and Campbell (1957) referred to it as the Fitzgerald Formation. The basal part of Middle Devonian succession in the south of the south shore of Great Slave Lake comprises evaporites, dolomite and dolomitic limestone breccia. The Chinchaga formation is overlain by a variety of Middle Devonian rock units, the Little Buffalo Formation in the south, the varied facies of Pine Point Formation in the central part and by the Lonely Bay Formation in the north. Mainly gypsum along with dolomite and dolomitic limestone constitutes the Chinchaga as a stratigraphic unit. A little limestone occurs near the base of Chinchaga Formation and has been called Hay Camp Member. The thickness of the Chinchaga Formation in the southern region may be in the order of 430 feet (Norris 1965).

Little Buffalo Formation -

The unit is named after Little Buffalo River where it is exposed. This unit consists of two main rock types designated as "dolomite" and "upper limestone dolomite". Lower dolomite is pale to dark brown, medium grained and massive in nature while upper dolomitic limestone is fossiliferous and granular with shale partings. The Little Buffalo Formation is overlain by evaporites of the Nyarling Formation but the contact is unexposed, (Norris, 1965).

Pine Point Formation -

The name Pine Point Limestone was proposed by Cameron in 1918 and was applied to strata exposed at Pine Point on the south shore of the Great Slave Lake. Pine Point Formation is the most variable unit of the Middle Devonian period and contains at least five or more distinct facies (Norris, 1965). The unit may be defined as the rocks occupying the stratigraphic interval between the top of the evaporites of the Chinchaga Formation and the base of the coarse dolomite of the Presqu'ile Formation

(restricted) or the base of the limestone of Sulphur Point Formation - stratigraphically equivalent to Presqu'ile Formation.

Pine Point Formation is composed of argillaceous limestone and dolomite with limy shale. Shales are bituminous and contain crinoids and brachiopod remains. The thickness of Pine Point Formation increases towards the north but decreases towards the south of Great Slave Lake probably due to approaching Elk Point evaporite basin (Campbell, 1957). In general it appears that Pine Point Formation varies rapidly in lithofacies from limestone to dolomite and as in the southeast of Great Slave Lake to gypsum, dolomite and limestone (Douglas, 1959).

Nyarling Formation -

The name Nyarling Formation was proposed for the unit which lies between Little Buffalo Formation (below) and Slave Point Formation (above), and contains mostly evaporites. The name of the unit is after Nyarling River - a major tributary of Little Buffalo River. Exposures are discontinuous and poor in the Pine Point area. Exposed outcrops consist of gypsum with minor amounts of fine grained limestone which contains carbonaceous streaks. The age of Nyarling Formation is Middle Devonian based on the stratigraphic interpretation since no evidence of fossil record was found in this unit.

Presqu'ile Formation -

Cameron (1918) proposed the name "Presqu'ile dolomite" for the strata exposed at Presqu'ile Point, this formation outcrops near Windy Point and Pine Point but exposures at Pine Point are not well developed except through mining operations. The data obtained through diamond drilling in this unit, gives a fair amount of information regarding the nature, facies and thickness of the formation. Nearly nine miles southeast of Presqu'ile Point on the south side of Great Slave Lake, one of the two major exposures of Presqu'ile Formation are seen. Probably this exposure covers a much larger area in this vicinity but is covered by a blanket of Pleistocene

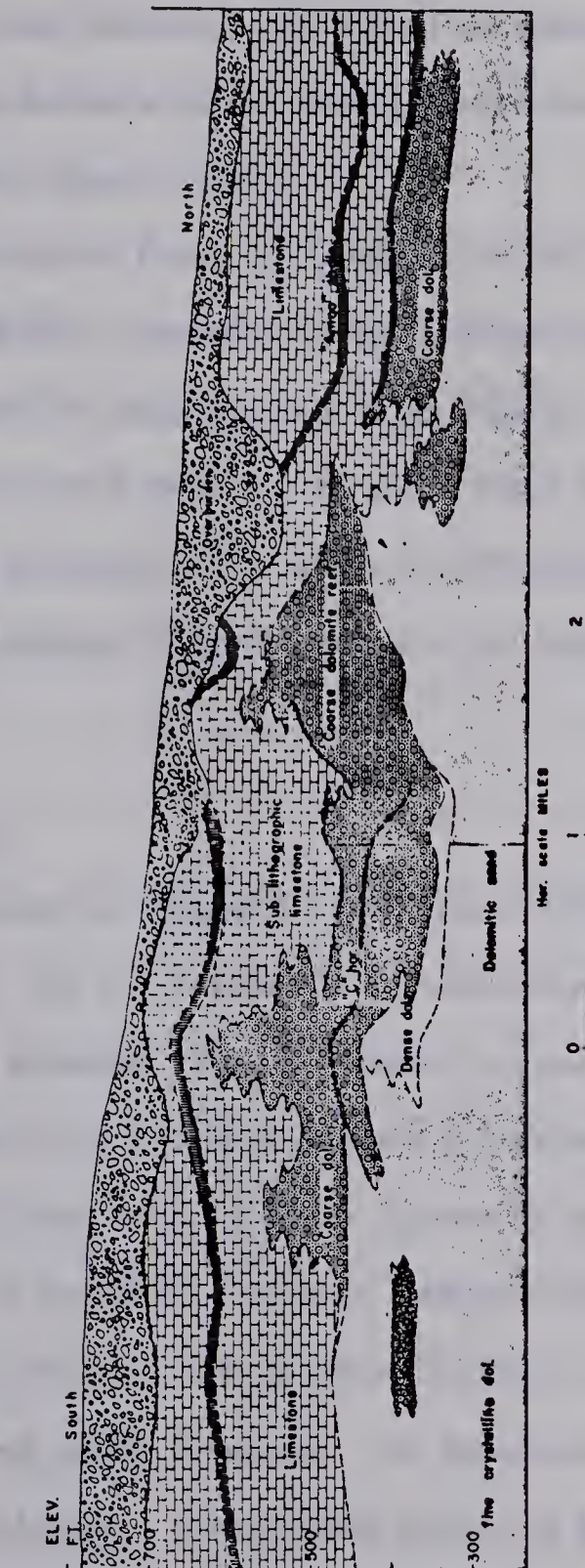


Figure 4.—A Section Across the Presqu'île Reef.
(After Campbell, 1966)

and Recent debris. The second major exposure is seen near Windy Point.

In the Pine Point vicinity the coarse, recrystallized dolomite appears to wedge out southward within fine grained dolomite (below) and limestone (above) (see Fig. 4).

It is presumed that this limestone probably passes into evaporites of the Nyarling Formation within a short distance. The Presqu'ile dolomite pinches out northward within fine grained dolomite (below) and limestone (above) along the south shore of Great Slave Lake (Norris, 1965).

The exposed outcrops of Presqu'ile Formation in the Pine Point area are commonly mottled light to brownish grey, coarse to medium grained, vuggy to cavernous and massive in nature. Lead-zinc mineralization is observed at places on the exposed outcrops and appears to be more abundant along the vague bedding planes. The maximum thickness is in the order of 230 feet in the Pine Point area as indicated by diamond drilling. The formation is fossiliferous and indicates a Middle Devonian age of deposition.

Sulphur Point Formation -

Sulphur Point Formation represents a sequence of limestone, interbedded limestone and dolomite. The unit is essentially undolomitized and appears to be equivalent of Presqu'ile dolomite. The unit overlies various formations of Pine Point unit and is in turn underlain by limestone of Slave Point Formation. In the Great Slave Lake region the Sulphur Point Formation appears to be present on the flanks of recrystallized dolomite of Presqu'ile Formation. Major facies comprise thinly and evenly bedded, cryptocrystalline, pale to brown limestone with carbonaceous streaks, argillaceous limestone and oolitic limestone. The formation is fossiliferous and contains Stringocephalus burtini - a brachiopod indicating Middle Devonian age.

Slave Point Formation -

The name "Slave Point Limestone" was proposed by Cameron in 1918, for

the upper part of the Middle Devonian succession exposed on the south side of Great Slave Lake. In the Pine Point area the base of Slave Point Formation is selected as the base of the Amco shale which is a marker bed restricted in its distribution. The Slave Point Formation consists of massive, quartzose, sandy limestone, light brown aphanitic limestone, thinly bedded fine grained limestone, coarse grained clastic limestone and dark grey, medium grained sandy limestone. In the southern part of the Great Slave Lake area the lower boundary of the Slave Point Formation is taken at the top of the evaporitic sequence of the Nyarling Formation. This stratigraphic unit is fossiliferous containing such diagnostic fossils as Emanuella sp. C and Emanuella sp. F which indicate a Middle Devonian age for this formation.

Hay River Formation-

The term Hay River was given by Cameron in 1918 to the beds exposed on and along Hay River. This formation is unconformably overlying the Slave Point Formation. In the Pine Point area the uppermost bedrock sections in some of the most westerly diamond drill holes comprise greenish limy shale and are believed to be the part of thick Hay River Formation. The available information suggests a conformable relation between limy shale and underlying Slave Point Formation. The lithofacies of this unit comprise greenish-grey shale, siltstone, argillaceous limestone, limestone and dolomite. The formation is fossiliferous containing diagnostic fossils such as Ladogoides pax and Lingula spatulata which have been reported from the Upper Devonian beds of the lower part of Waterways Formation of northeastern Alberta. Thus Hay River Formation has been assigned an age of Upper Devonian.

Pleistocene and Recent Formation -

A considerable area in the Pine Point vicinity is covered by a mantle of glacial drift resulting from the Laurentide glaciation (Douglas, 1959). Besides glacial drift, coverage materials also comprise alluvial sands and silts derived from

Slave River, and post glacial raised beach deposits which afford excellent road material.

PALAEOPHYSIOGRAPHIC CONSTRUCTION

An account on palaeophysiographic conditions responsible for reef building has recently been given by Campbell (1966). In the light of available information regarding various lithofacies and their complex nature it is presumed that during the Palaeozoic period reef building activity took place in the area. Probably a sedimentary shelf was present between the Precambrian Shield in the northeast and Cordilleran Geosyncline in the southwest. Presumably, during this time several sets of orogenic movements caused some disturbance in the area. No appreciable deformation took place during a long period from Cambrian to Ordovician except for little deposition of shale, sandstone, limestone and dolomite. But close to Middle Devonian time the development of a marine basin began to take shape. This basin was stretched from the southern limits of northwestern Territories to the northern limits of Dakota. The shape of the basin was moreover like an inland sea which had an outlet at the northwest end. The deposition of shale and a carbonate complex took place in this basin. During this time conditions seem to have been quite favorable for extensive development of reef organisms which were responsible for building several reef complexes. The reef development was rather fast in the northwest region where the inland sea had an opening into the Arctic Ocean. This fast growth of reef restricted the marine circulation to such an extent that the flow of seawater into the basin became inadequate to replenish evaporation loss. The salinity of the inland sea increased correspondingly with the increasing rate of evaporation.

Prior to complete evaporation, anhydrite and a little dolomite was precipitated. Following period passed through a phase of precipitation of sodium, potassium and magnesium chlorides on this vast area causing the formation of Prairie evaporites.

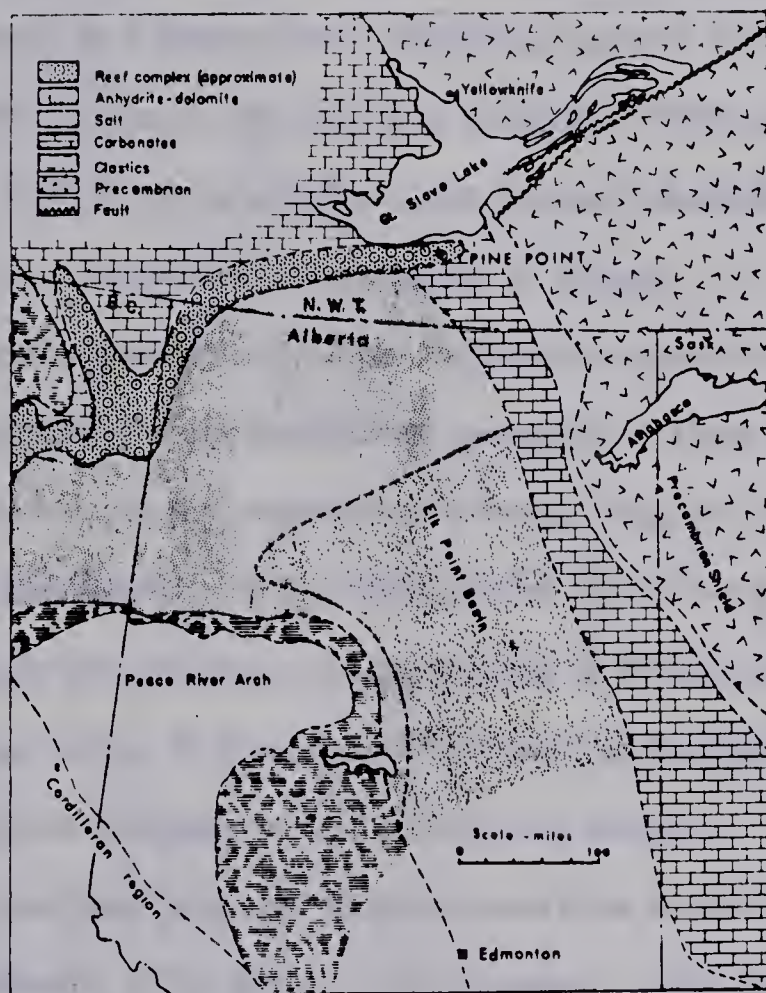


Figure 5.—Approximate distribution of Upper Elk Point (Middle Devonian) lithofacies with respect to the Precambrian Shield and the Pine Point Ore Deposits.

(After Campbell, 1966)

STRUCTURAL PATTERN

The Great Slave Lake basin is distinct in lithology as well as in structure from its neighbouring geological provinces. The rock units comprising volcanic and sedimentary formations in the eastern arm of the lake could be divided into three main groups which are separated by two major unconformities (Burwash, 1957). While two older groups are folded, intruded and levelled by subsequent erosion, the youngest one is gently dipping and close to major fault zone. The basement complex is intruded by granite, diorite and diabase and is broken by several sets of joints and northwesterly trending fault systems. According to Douglas (1959) these faults are mainly linear features with minor en'echelon along the south eastern edge of the Great Slave Lake. They show considerable displacement at places.

The Middle Devonian and older Palaeozoic rocks of the Great Slave Lake region are responsible for the homoclinal succession. These beds dip gently towards the southwest with a general northwesterly trend. Regional slope of the Precambrian basement is 20 feet per mile in the south side of Great Slave Lake. Local variations are not infrequent and indicate a westerly slope of 30 feet per mile and sometimes even 125 feet per mile. It is presumed that much of the folding is the result of differential compaction between on reef and off reef deposits.

These prominent basement features constitute several fault systems trending southwest (Stockwell, 1936; Brown, 1950; Burwash, 1957; Douglas, 1959; Norris, 1965) and could be traced for at least 200 miles beneath the Palaeozoic sediments. Recent drilling and aeromagnetic data indicate a similar set of faults trending southwest immediately west of the Pine Point area.

As interpreted these faults show the lines of weakness on which Palaeozoic and Post-Palaeozoic movement is suspected. In the nearby area of Slave River delta three major fault systems trending NE can be traced to the western limits of Precambrian exposures (Burwash, 1957, Fig. 6). Subsequent recurrent movement

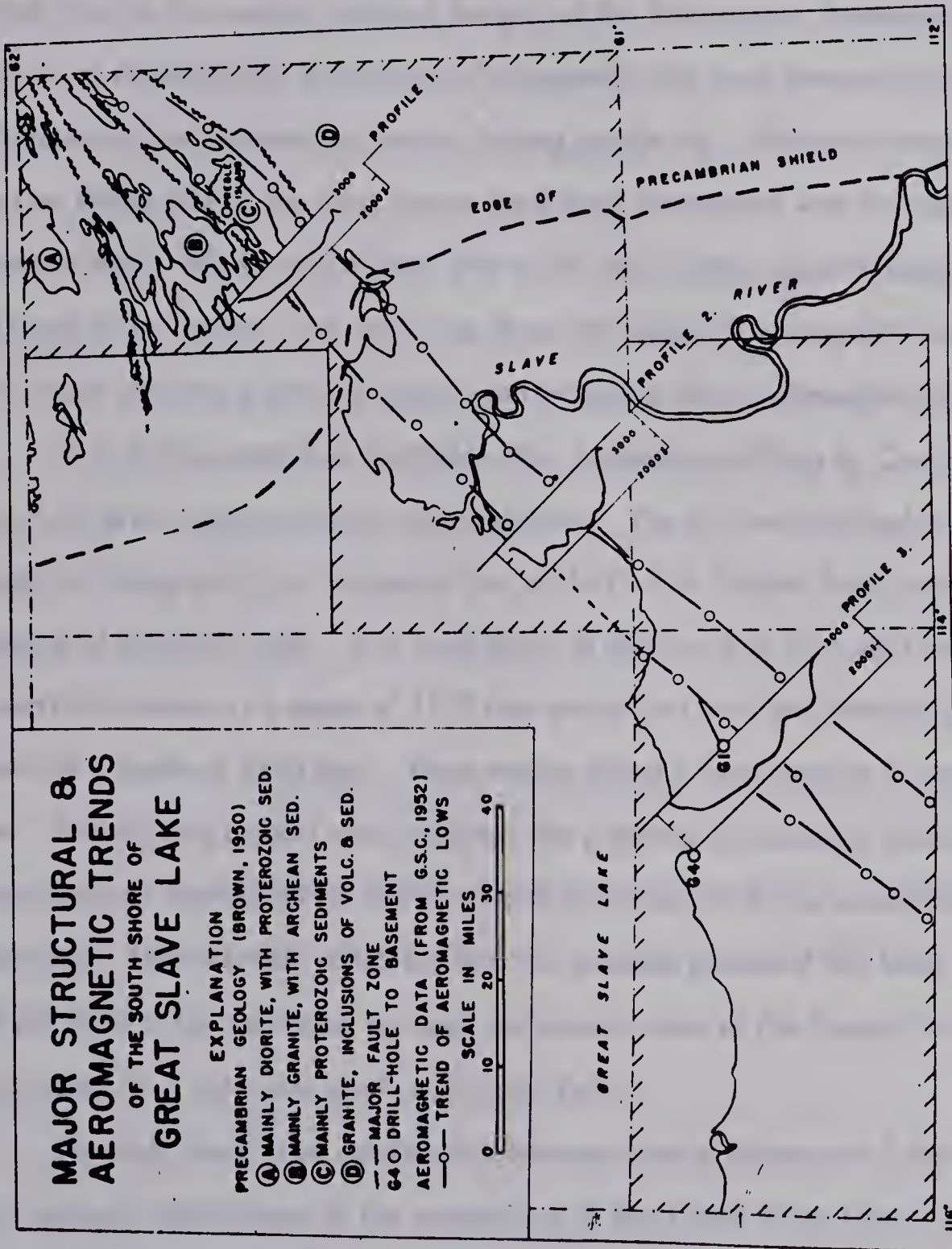


FIG. 6.—Aeromagnetic trends and major structural features along south shore of Great Slave Lake.
(After Burwash, 1957)

and erosion of these faulted blocks resulted in the formation of a structural graben along the southern limits of the Great Slave Lake. The floor of the graben is dipping gently and is composed of quartzite and conglomerate but the walls are of granitic to gneissic composition. The aeromagnetic data suggest an extension of this fault system towards the western exposed margins of the Precambrian Formations. In the vicinity of Preble Island indications of a magnetic low were observed which suggest a Proterozoic and sedimentary terrain having gentle dip. Different patterns of structures on either side of the fault system have been interpreted with the help of aeromagnetic data. While on the south side of the fault system several magnetic highs are found to be present, the north side shows the presence of magnetic lows. The magnetic highs indicate a granitic terrain and magnetic low a sedimentary terrain.

The drilling data now available after subsurface drilling by Cominco Ltd. in Pine Point area, suggest similar interpretations. The G-1 well drilled at Pine Point affords an interpretation of magnetic low while G-4 at Sulphur Point indicates the presence of magnetic high. It is worthwhile to mention that G-1 well encountered a quartzitic terrain at a depth of 1173 feet while G-4 well encountered a granitic terrain at a depth of 1343 feet. These results afford a confirmation for aeromagnetic data. This drilling project also indicated the presence of numerous closely spaced gentle flexures forming minor anticlines and synclines, and also several faults of low magnitude. Norris (1965) indicated that the average plunge of the folds is 22.6 feet per mile to the southwest between the eastern edge of the Presqu'ile Formation and a point 13.7 miles due south of Sulphur Point.

Probably there is no relationship between gentle Palaeozoic folding and major tectonic disturbance in the eastern arm of the Great Slave Lake. But the minor scale deformations of the Palaeozoic sediments in the Pine Point area might have been caused due to some kind of Post Devonian movement. It seems that the period of major deformation was restricted to Precambrian but might have continued throughout the Middle Devonian period considerably at low magnitude.

CHAPTER - III

GEOOTHERMOMETRIC CONSIDERATIONS

Several methods for estimating temperatures of geological processes have been developed and used in recent years. Of these, two methods that have been used increasingly during the past few years in predicting the temperature of formation, are the study of liquid inclusions in minerals and determination of iron content of sphalerite. Besides, the determination of fractionation of stable isotopes in different mineral assemblages has been developed and proved useful.

In the present investigation the iron content of sphalerite in Pine Point sulfide assemblage was determined. Oxygen isotope geothermometry has been utilized in this study and will be discussed in a separate section. Thin sections of sulfide ores and more especially sphalerite sections were examined for inclusions, but no encouraging results were obtained from the present set of samples. An attempt was also made to determine the magnesium content in solid solution in calcites related to the orebodies in order to estimate temperature of formation of these carbonates.

DETERMINATIONS OF IRON CONTENTS OF SPHALERITE

The iron content of sphalerite samples was determined by chemical and x-ray fluorescence methods. An account of sample preparation and techniques used is given in Appendix II.

Results - The results obtained in this study are presented in Table 2 and 3. Sphalerite samples analyzed contain a minimum of 0.7 mole per cent FeS and a maximum of 15.8 mole per cent FeS in ZnS. It is well understood that iron substitutes for zinc in the sphalerite structure. Kullerud (1959) calculated that a maximum of 4.5 mole per cent FeS can enter the ZnS lattice at 140°C and a maximum of about 39 mole

Table 2. Measurements of Mole Percent FeS in sphalerites from Pine Point Ore field,
N.W.T., Canada

S.No.	Sphalerite No.	Wt. of sample (gms)	Wt. Fe in sample (mgs)	Wt. ZnS in sample (gms)	Moles ZnS	Wt. FeS in sample (gms)	Moles FeS	Mole % FeS
1.	P 29 Dk. coloured	0.5252	48.2	0.4493	0.004610	0.0759	0.000863	15.8
2.	P 29 Lt. coloured	0.4915	14.0	0.4695	0.004820	0.0220	0.000250	4.9
3.	N-42-C-1 Dk. coloured	0.4057	10.5	0.4866	0.004990	0.0181	0.000206	4.0
4.	N-42-C-1 Lt. coloured	0.4388	1.7	0.4361	0.004480	0.0027	0.000031	0.7
5.	N-42-C-3 Dk. coloured	0.5458	7.6	0.5338	0.005480	0.0120	0.000136	2.4
6.	N-42-C-3 Lt. coloured	0.6316	7.0	0.6206	0.006370	0.0110	0.00125	1.9
7.	N-42-C-4 Dk. coloured	0.6012	10.2	0.5851	0.006000	0.0161	0.000183	3.0
8.	N-42-C-4 Lt. coloured	0.2563	3.5	0.2508	0.002570	0.0055	0.000063	2.4
9.	O-42-C-1 Lt. coloured	0.5328	5.0	0.5249	0.005390	0.0079	0.000090	1.6

Table 3-A. Mole % FeS and estimated Temperatures /°C for Pine Point Sphalerites.

S. No.	Sample No.	Mole % FeS		Ave. Mole % FeS	Est. temp. /°C
		Hexachlorferrate Method*	X-ray Fluorescence Method+		
#	P 29				
1.	Dk. sphalerite	15.80	Considered as standard		490°C
2.	Lt. sphalerite	4.90	7.37	6.2	280°C
#	N-42-C-1				
3.	Dk. sphalerite	4.00	5.06	4.5	260°C
4.	Lt. sphalerite	0.70	1.11	1.0	100°C
#	N-42-C-3				
5.	Dk. sphalerite	2.40	5.06	3.8	220°C
6.	Lt. sphalerite	1.90	2.98	2.5	175°C
#	N-42-C-4				
7.	Dk. sphalerite	3.00	8.29	5.7	285°C
8.	Lt. sphalerite	2.40	3.90	3.2	200°C
#	O-42-C-1				
9.	Lt. sphalerite	1.60	3.90	2.8	185°C

Table 3-B. Mole% FeS and estimated temperatures /°C for Pine Point Sphalerites.

S. No.	Sample No.	Mole % FeS		Ave. Mole % FeS	Est. temp. /°C
		Hexachlorferrate Method*	X-ray Fluorescence Method x		
#	P 29				
1.	Dk. sphalerite	15.80	Not considered		
2.	Lt. sphalerite	4.90	Considered as standard		260°C
#	N-42-C-1				
3.	Dk. sphalerite	4.00	1.44	2.87	170°C
4.	Lt. sphalerite	0.70	0.34	0.57	70°C
#	N-42-C-3				
5.	Dk. sphalerite	2.40	1.60	2.00	160°C
6.	Lt. sphalerite	1.90	0.98	1.44	140°C
#	N-42-C-4				
7.	Dk. sphalerite	3.00	3.46	3.23	200°C
8.	Lt. sphalerite	2.40	1.22	1.81	150°C
#	O-42-C-1				
9.	Lt. sphalerite	1.60	1.19	1.39	140°C

* Chemical analyses by A. Stelmach, Chemist, Department of Geology, University of Alberta.

+ X-R-F calculations using high value 15.80 mole % as highest peak.

x X-R-F calculations using lower value 4.90 mole % as highest peak.

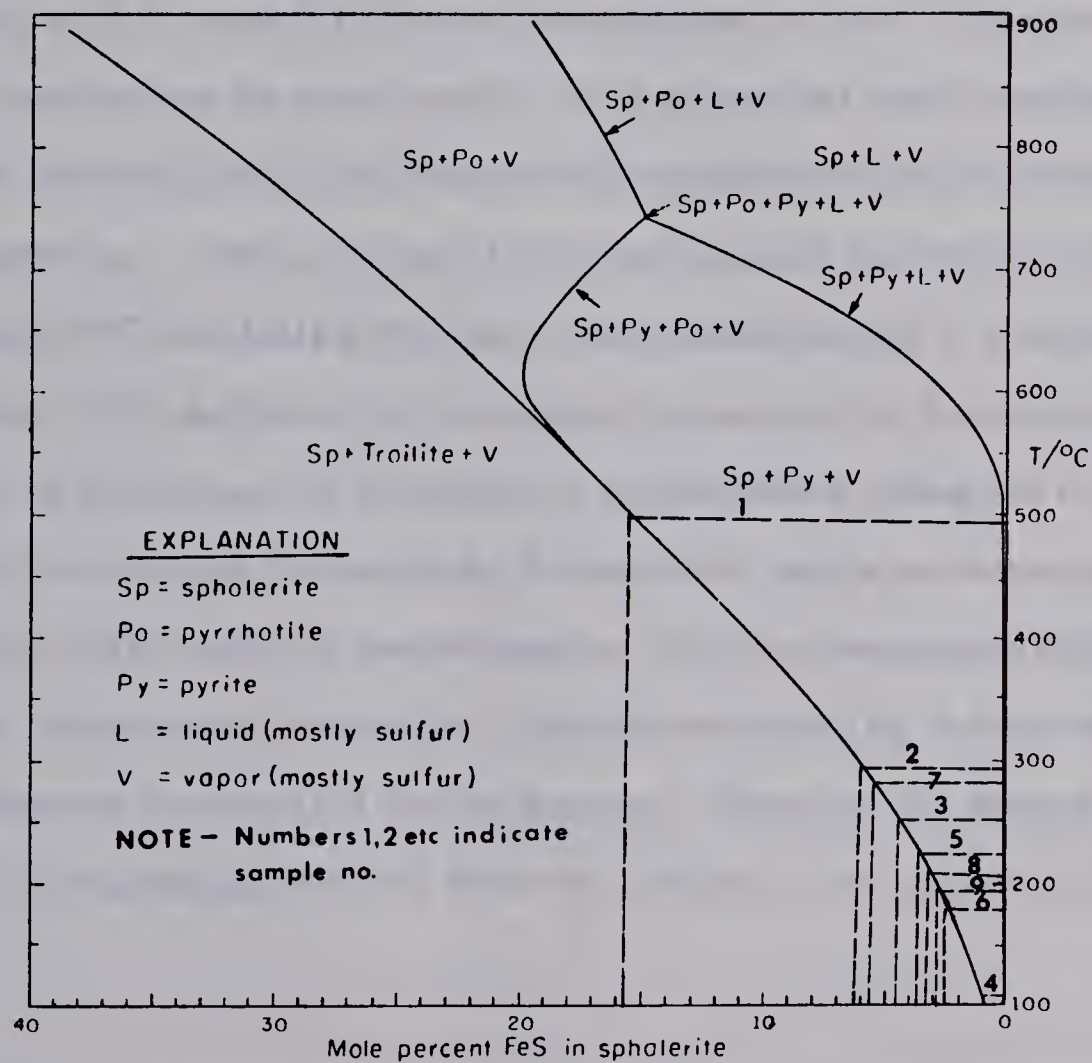


FIG.7- Mole% FeS in ZnS and estimated temperature for Pine Point Sphalerites.

(After Sims and Barton)
1961

per cent FeS can be tolerated in the ZnS lattice at 894°C provided iron is available in excess to the system. It is also known now that the iron content of sphalerite decreases with the decrease in formation temperature. In the present study the formation temperatures were calculated with the help of FeS-ZnS equilibrium diagram given by Sims and Barton, Jr. (1961). A temperature range of 100° to 490°C is obtained for Pine Point sphalerites (Fig. 7, Table 3-A). The maximum concentration of FeS in sphalerite was found in sample no. P 29, dark coloured sphalerite. This high concentration (amounting to 15.8 mole % FeS) seems rather unusual in view of the general trend of the other samples from the same locality. If we assume that results obtained for this sample are rather high due to an undetectable contamination and not reliable to consider temperature limits, the rest of the samples present the formation temperatures well below 260°C (see Table 3-A), that is more appropriate and is in accordance with other studies which indicate a low to moderate temperature for this mineralization. The results of dark coloured P 29 sample are of questionable nature and for the present consideration we assume that results for this particular sample are erroneous.

Zinc sulfide occurs in two polymorphs, cubic low-temperature sphalerite and hexagonal high-temperature wurtzite. Wurtzite was looked for in these samples by x-ray diffraction technique but was not detected. Therefore, the absence of wurtzite in the sulfide assemblage from Pine Point also indicates a low temperature mineralization.

FACTORS INFLUENCING THE IRON CONTENTS OF SPHALERITE

The determination of temperature by the iron contents of sphalerite requires equilibrium between ZnS and FeS at the time for which the temperature is to be determined. There are essentially four factors which are responsible for the variation in iron contents of sphalerite.

1. Temperature
2. Total pressure
3. Sulfur activity or chemical potential of sulfur.
4. Effect of solid solution

As indicated by Kullerud (1959), at equilibrium, the sphalerite has the composition of the solvus of the FeS-ZnS system for that temperature. The solvus used here is after Sims and Barton Jr. (1961).

The average temperature for Pine Point sphalerites calculated with the help of this solvus is 160°C (see Table 3-B, neglecting the P 29 Dk. sphalerite value).

In addition to temperature, the solubility of FeS in ZnS depends on total pressure, because of the volume increase in the formation of iron rich sphalerite from ZnS and FeS (Rose, 1961). A pressure correction of about 25°C per 1000 bars total pressure was calculated by Kullerud, who showed with the help of his experimental data that increasing pressure decreases the solubility of FeS in ZnS.

The third significant factor which has an influence on the FeS content of sphalerite is the partial pressure or the activity of sulfur in the system at the time of equilibrium. The activity of sulfur is explained by Sims and Barton Jr. (1961) in pyrite-sphalerite assemblage. The following equation given by them explains the importance of this activity.



From their experimental results, Sims and Barton Jr. suggested that at constant temperature within the pyrite-sphalerite stability field, an increase in the chemical potential of sulfur by two orders of magnitude decreases the mole per cent of FeS in ZnS by one order of magnitude. It is now well understood that the range in the composition of FeS - saturated sphalerite is only about one order of magnitude, say 39 mole % at 894°C to about 3 mole % at 200°C, whereas the range of the chemical potential of sulfur in pyrite-sphalerite is many orders of magnitude. This relationship,

therefore, indicates the importance of the activity of sulfur in temperature interpretation of pyrite-sphalerite assemblages.

Similarly, in pyrrhotite-sphalerite assemblage the activity of sulfur is an important factor. Pyrrhotite in nature is slightly deficient in Fe relative to the composition FeS. Kullerud found no appreciable effect on the Fe content of ZnS as long as pyrrhotite was associated with sphalerite in the system (Kullerud, 1953). But Barton and Kullerud in a later publication (1957) indicated that in the absence of pyrrhotite, the sulfur activity in pyrite-sphalerite system is progressively increased. Recently Barton and Toulmin (1966) explained the phase relations involving sphalerite. They worked out the equilibrium diagrams for the Fe-Zn-S system for a temperature of 380° to 850°C.

In a sphalerite-pyrite and pyrrhotite assemblage, the composition of sphalerite changes from 13 mole per cent FeS at 742°C to 10 mole % FeS at 580°C. Their studies also indicate the difficulty in extrapolating this equilibrium to lower temperatures and they concluded that the use of this assemblage for quantitative geothermometry is not feasible at present. The fluctuations of sulfur fugacity influences the iron content of sphalerite and are responsible for growth zoning in sphalerite. They also stated that the experimental and theoretical work invalidates the wide use of binary system FeS-ZnS as a geothermometer though permitting quantitative geothermometry based on the FeS content of sphalerite in appropriate assemblages. (Toulmin and Barton, Nov. 1966).

Discussion-

The ore assemblage at Pine Point is mainly of galena-sphalerite-pyrite-marcasite type. A little pyrrhotite is observed in association with pyrite and marcasite in one of the studied polished sections. The paragenetic sequence indicates earlier precipitation of pyrrhotite subsequently followed by pyrite-marcasite, sphalerite and galena. Pyrite and marcasite show complex intergrowths and it seems they precipitated simult-

aneously. The details regarding textural relationships and paragenetic order of deposition will be discussed in the following chapter. The important ore minerals are galena and sphalerite. Pyrite and marcasite are nearly ubiquitous. Pyrrhotite is rarely seen. The temperature classification of the deposits by sulfide minerals assemblage suggests that a range of temperature not exceeding 260°C brought about this mineralization.

In the present study a range of FeS content in ZnS is found to 0.57 mole % to 15.8 mole % (see Table 3-A and B). However, the validity of the maximum value of 15.8 mole % is questionable. The variation in FeS content in ZnS, may in part be related to the temperature of formation; changes of pressure seem most likely to be responsible for most of the variation.

The problem of equilibrium is rather difficult to explain since present data is limited but on the basis of examination of the polished sections and information obtained from other studies of these samples, it is understood that the equilibrium was attained at least twice during the period of mineralization. No information on the sulfur activity and its subsequent affect on the precipitation of Pine Point sulfides is available at present.

Significantly, in one of the sphalerite samples of the present study a zone with an FeS content of 2.87 mole % indicating a temperature limit of 170°C overlies a zone with 0.57 mole % FeS having a temperature limit of 70°C (see Table 3-B). This type of relationship has been observed in all sphalerite samples in the present study. Zones are separated by sharp demarcation lines. It is also seen that the bands of relatively iron deficient sphalerite are surrounded by bands of iron rich sphalerite. This arrangement of the zones possibly indicates that either the time during which the temperature of 170°C was maintained was so brief that no perceptible diffusion from one zone to other took place or some other factor was affecting the iron content of sphalerite. A reverse arrangement of zones was also seen in a few polished sections.

A number of thin sections of sulfide ores were examined for possible fluid inclusions. Except for P 29 ore sample, none of the studied sections indicated the presence of fluid inclusions. The fluid inclusions present in this section are very minute, elongated and spherical in outline. They are very few in number and only two of them could be seen clearly with the help of the microscope. However, their presence in Pine Point ore samples is certain. The present set of samples did not yield very definite results but indicated further possibilities for the detailed study which may assist in measuring the temperature of the formation of these sphalerites.

DETERMINATION OF MINOR ELEMENTS IN SULFIDES

The determination of minor elements in relation to the temperature of formation of sulfides has been attempted by many workers (Gavelin and Gabrielson, 1947; Maserlandt and Schroll, 1954). Fleischer (1955) is of the opinion that many generalizations do support some kind of linkage between minor element concentration and temperature of formation. For example, there is a strong tendency for high gallium, high germanium and low indium in sphalerites from Mississippi valley lead-zinc deposits which are formed at low temperature.

Considering the possibility of obtaining some information regarding temperature of formation, an effort has been made to determine minor elements present in Pine Point sulfides.

Qualitative analyses of twenty-eight samples was done using x-ray fluorescence method to obtain comparative amounts of minor elements in Pine Point sulfides. An order of sensitivity is used to indicate low, poor and trace x-ray spectrographic limits while such comparison is made.

Results - X-R-F analyses of Pine Point sulfides indicate the presence of Se, Sb, Cd, Cu, Mo, Sn, Bi, Mn, Ga, Ge and In as minor elements in addition to Fe, Pb, Zn as major elements. Results are summarised in Table 4-7.

Table 5. Minor elements in Galena and Marcasite Samples, Pine Point Ore field, N.W.T., Canada.

Symbols represent: R = Qualitative Analysis, X = Elements Present, A = Elements absent but looked for.

S. No.	Mineral	Sample No.	Type of Data	Pb	Fe	Zn	Sn	Cd	Sr	Mo	Sb	Se	Bi	Remarks
1.	Galena	P 29	R	X	A	X	X	X	A	X	X	A	A	Separated galena only
2.		N-42-C-1	R	X	A	X	X	X	A	X	X	X	X	"
3.		N-42-C-3	R	X	A	X	X	X	A	X	X	A	X	"
4.		O-42-C-1	R	X	A	X	A	X	A	A	X	A	X	"
5.	Marcasite	O-42-C-1	R	X	X	X	A	X	A	X	X	X	X	Separated marcasite only
6.		N-42-C-4	R	X	X	X	A	A	A	X	X	X	X	"

Table 6. Minor Elements in Sulfide Ores, Pine Point Ore field, N.W.T., Canada.

Symbols represent: R = Qualitative Analysis, X = Elements present, A = Elements absent but looked for.

S. No.	Sample No.	Type of Data	Pb	Zn	Fe	Sb	Se	Cd	As	Bi	Mn	Ge	Ga	In	Cu	Mo	Sn	Remarks
1.	N-42-C-1	R	X	X	X	X	X	X	A	A	A	A	X	A	A	X	A	Ore sample
2.	N-42-C-2	R	X	X	X	X	X	X	A	A	A	A	A	A	A	A	A	"
3.	N-42-C-3	R	X	X	X	X	X	A	A	A	A	X	X	A	A	A	A	"
4.	N-42-C-4	R	X	X	X	X	A	A	A	A	A	A	A	A	A	X	X	"
5.	N-42-C-5	R	X	X	X	X	A	X	A	A	A	A	X	A	A	X	A	"
6.	PP-A	R	X	A	X	X	X	A	A	A	A	X	A	A	A	A	A	"
7.	PP-B	R	X	A	X	X	A	A	A	A	A	X	A	A	A	A	X	"
8.	PP-M	R	X	X	X	X	X	A	A	A	A	A	X	A	A	X	A	"
9.	WP	R	X	X	X	A	A	A	A	A	A	A	A	A	A	A	X	"

Table 7. Minor Elements in Pyramid Sulfides, Pine Point Ore field, N.W.T., Canada

Symbols represent: R = Qualitative Analysis, X = Elements present, A = Elements absent but looked for.

S. No.	Sample No.	Type of Data	Zn	Fe	Pb	Se	Sb	As	Cd	Ag	Bi	Mn	Ge	Ga	In	Remarks
1.	PRM-1	R	X	X	X	X	X	A	X	A	A	A	A	A	A	Ore sample
2.	PRM-2A	R	X	X	X	X	X	A	A	A	A	A	A	A	A	"
3.	PRM-2B	R	X	X	X	X	A	A	X	A	A	X	A	A	A	"
4.	PRM-2B	R	X	X	X	X	A	A	X	A	A	X	A	A	A	"

Discussion - It is generally understood that the concentration of an element will be governed by its availability and by the ability of the host mineral to accommodate it. The first of these factors is governed by the activities of different minerals already present in ore forming solutions, the second by the nature of the host mineral. Both factors are influenced by the temperature and pressure changes (Fleischer, 1955).

Undoubtedly, Mn, Cd, Sn, Cu, Pb, Fe and Se can substitute Zn and S in sphalerite lattice. Probably Ga, Ge and In, and possibly Mo and Bi may also substitute for zinc. Galena can easily accommodate Cd, Sb, Bi, Mo, Mn, in addition to Fe, Se, Sn and Zn. Pyrite and marcasite lattice can also accommodate Cu, Se, Cd, Ga, Ge and In (see Table 8), but their distribution is limited and much depends on the other factors affecting mineralization (Fleischer, 1955).

Interpretation of minor elements associated with Pine Point sulfides indicates relatively low temperature of formation. Elements Se, Sb and Cd show significant distribution while elements Cu, Mo, Sn, Bi, Mn, Ga, Ge and In show less significant distribution.

All samples of sphalerite, one pure galena and two marcasites indicate presence of low selenium in them. Little is known about the geochemistry of selenium in sphalerite but it is definite that a certain amount of selenium does substitute for sulfur in Zn lattice. It seems selenium has been derived from the shale and bitumen present in the Pine Point area as selenium content varies with organic matter (Bett et al, 1939).

It seems antimony has uniform distribution throughout Pine Point sulfides and occurs only in trace amount. This accords with the conclusions derived by Tischendorf (1955) that the antimony content decreases with decreasing temperature.

The study of Pine Point sulfides indicated a better distribution of cadmium. The spectrographic sensitivity is "poor" as compared to antimony. Many workers expressed that cadmium content of sphalerite seems to be independent of the condition of formation (Ottedal, 1940; Stoiber, 1940; Gabrielson, 1945) but Kutina (1953)

Table 8. Apparent ionic and covalent radii of the elements present in Pine Point Sulfides. (After Ahrens, 1952 and Pauling, 1940).

S.No.	Element	Symbol	Ionic radius (A) Valence	Radius	Covalent Radius (A)
1.	Antimony	Sb	+3	0.76	1.41
2.	Bismuth	Bi	+3	0.96	1.46
3.	Cadmium	Cd	+2	0.97	1.48
4.	Copper	Cu	+1	0.96	1.35
	Copper	Cu	+2	0.72	-
5.	Gallium	Ga	+3	0.62	1.26
6.	Germanium	Ge	+2	0.73	1.22
	Germanium	Ge	+4	0.53	-
7.	Indium	In	+3	0.81	1.44
8.	Iron	Fe	+2	0.74	1.23
	Iron	Fe	+3	0.64	-
9.	Lead	Pb	+2	1.20	1.46
10.	Molybdenum	Mo	+4	0.70	1.38
	Molybdenum	Mo	+6	0.62	-
11.	Manganese	Mn	+2	0.80	-
12.	Selenium	Se	-2	1.98	1.17
13.	Sulfur	S	-2	1.84	1.04
14.	Tin	Sn	+2	0.93	1.42
	Tin	Sn	+4	0.71	1.40
15.	Zinc	Zn	+2	0.74	1.31

observed that amount of cadmium decreases with increasing temperature.

The presence of Ga, Ge and In in Pine Point sulfides is of interest. There is a general agreement among many workers (Gabrielson, 1945; Ottedal, 1940; Schroll, 1953) that gallium and germanium contents are most likely to be high in sphalerites from low temperature deposits such as those of Mississippi Valley type. However, present data in case of Pine Point sulfides is limited and it is only possible to conclude that germanium and gallium contents are relatively higher as compared to indium in these sulfides. The Pine Point sulfides show only traces of indium and since indium contents increase with increasing temperature (Fleischer, 1955) the mineralization in our case seems to have taken place at low temperature.

Only two Pyramid sulfides contain manganese as indicated by "poor" spectrographic sensitivity. The manganese content varies with the iron content and hence it is expected to be high in high temperature deposits (Urbain, 1910; Stoiber, 1940; Schroll, 1948; Fryklund and Fletcher, 1955). In the present case manganese seems to be fairly low which indicates low temperature of formation.

The x-ray spectrographic sensitivity indicates a trace amount of tin and molybdenum. Molybdenum seems to be present due to Mo target radiation tube used for X-R-F analysis. None of the sphalerite samples indicated the presence of molybdenum. Since greater amounts of tin expected in the deposits of high temperature (Stoiber, 1940; Warren and Thompson, 1945), the Pine Point sulfides could be regarded as low temperature deposits. Kullerud (1953) arrived at similar conclusions from his study of 54 sphalerites.

Only trace amount of copper and bismuth is present in the present case. Four samples of sphalerite indicated presence of copper while none of the galena or marcasite samples studied here indicated any copper. Bismuth present in Pine Point sulfides indicates only trace amount and seems to be a mineral impurity.

In brief it is possible to conclude from the foregoing discussion and interpretation that Pine Point mineralization most likely took place at relatively low temperature.

DETERMINATION OF MAGNESIUM CONTENT IN CALCITE

An effort was made to determine Mg present as MgCO_3 in solid solution in Pine Point calcites. In all, 17 calcite samples were analysed using standard x-ray diffraction technique to interpret whether or not there is any shift in calcite peaks. The experiment conducted in this case is partially based on the earlier studies done by Harkar and Tuttle (1955) to determine the limits of solid solution along the binary join $\text{CaCO}_3\text{-MgCO}_3$. They examined the subsolidus relations in the system $\text{CaCO}_3\text{-MgCO}_3$ between 500 – 900°C using synthetic calcites grown in equilibrium with dolomite. During their investigations they observed a relative shift in calcite peaks to higher angles, i.e. towards the corresponding peaks of magnesite. Their results confirmed that some calcium in calcite was replaced by magnesium and, therefore, the shift in calcite peaks was a function of magnesium content.

In the present study in order to calculate the relative shift in calcite peaks, two convenient standards, silicon and solidum chloride (halite), were mixed with each sample of calcite. The proportion of the mixture i.e. – carbonate, silicon and sodium chloride was maintained at 2 : 3 : 1. The samples were run on x-ray diffraction using copper radiation to find relative positions of the peaks. Each sample was run three times to assure the accuracy of results. The mean value of the three peaks was taken in each case to measure the correct angular distance to $\pm 0.01^\circ$ of 2θ ($\text{CuK}\alpha$) between the peaks. For the purpose of this measurement, the point in the center and half the height of the peaks in question was used throughout the calculation. The difference in 2θ (and) between the positions of carbonate peaks ($2\theta_c - 2\theta_s$) was calculated and presented in Table 9.

Results and Discussion-

Harkar and Tuttle (1955) found that the angle $2\theta_c - 2\theta_s$ increases with the temperature. Assuming that the Pine Point calcites were grown in equilibrium with

Table 9. Measurement of the peak positions for Pine Point calcites with reference to standards.

S. No.	Sample No.	Mean Peak Positions in $2\theta^\circ$			Shift in Peak ($2\theta^\circ$)		Remarks
		Standards Used			Si $2\theta_c - 2\theta_s$	NaCl $2\theta_c - 2\theta_s$	
		Si	NaCl	calcite			
1.	PP 2	0.08	0.96	0.96	0.01	0.00	calcite
2.	PP 4	0.10	0.10	0.10	0.00	0.00	calcite
3.	PP 6	0.10	0.09	0.10	0.00	0.00	calcite
4.	PP 8	0.08	0.10	0.08	0.00	-	calcite
5.	PP 9	0.10	0.10	0.10	0.00	0.00	calcite
6.	PP 10	0.08	0.10	0.10	0.02	0.00	calcite
7.	PP 11	0.09	0.10	0.10	0.01	0.00	calcite
8.	PP 14	0.08	0.09	0.09	0.01	0.00	limestone
9.	PP 17	-	0.09	0.10	-	0.01	calcite with trace dolomite
10.	PP 18	-	0.10	0.10	-	0.00	calcite with trace dolomite
11.	PP 20	0.09	0.10	0.10	0.01	0.00	limestone
12.	PP 20	-	0.10	0.09	-	-	calcite with trace dolomite
13.	PP 23	0.09	0.10	0.10	0.01	0.00	calcite
14.	PP 24-A	0.09	0.10	0.10	0.01	0.00	calcite with trace dolomite
15.	PP 26-B	-	0.10	0.10	-	0.00	"
16.	PP 27	-	0.10	0.10	-	0.00	"
17.	PP 34	0.08	0.10	0.10	0.02	0.00	limestone

$2\theta_c = 2\theta$ for calcite

$2\theta_s = 2\theta$ for standard

dolomite, the relative shift of calcite peaks with that of standards was calculated and it was found that either there is no shift in calcite peak or so little as to be considered negligible. The values for such shift in calcite peaks with reference to standards have a range of 0.00 to 0.01° which is practically inadequate to permit further calculations by making use of graphs given by Harker and Tuttle. Since the difference of $2\theta_c - 2\theta_s$ in the case of Pine Point calcites is extremely low, the magnesium contents present in calcite could not be calculated and consequently, no further calculation for temperature limits are possible. At present it is only feasible to infer from this study that Pine Point carbonate were formed at low temperature.

CHAPTER IV

INTERPRETATION OF ORE TEXTURES

Based on the detailed study of 30 ore samples from Pine Point orefield, the mineralogical relationship, textural interpretation and possible paragenesis is suggested. The textural terminology is more or less restricted to available terms and wherever it is not practicable due to complex arrangement of different minerals a suitable description to this effect is given. As far as possible no new textural term is coined in order to avoid duplication and overlapping.

MINERALOGICAL RELATIONSHIP-

The microscopic examination of polished and thin ore samples from Pine Point orefield revealed the presence of the following minerals.

- | | | |
|----|--|-----------------|
| 1. | Pyrite----- FeS_2 | |
| 2. | Pyrrhotite----- Fe_{1-x}S | |
| 3. | Marcasite----- FeS_2 | ORE MINERALS |
| 4. | Sphalerite----- ZnS | |
| 5. | Galena----- PbS | |
| | | |
| 6. | Dolomite----- $\text{CaMg}(\text{CO}_3)_2$ | GANGUE MINERALS |
| 7. | Calcite----- CaCO_3 | |

Their mineralogical characteristics are summarised in Table 10.

TEXTURAL RELATIONSHIP-

A detailed mineralographic study of Pine Point sulfides reveals the following

Table 10. Mineralogical Characteristics of minerals present in Pine Point Ores.

S. No.	Minerals	Chem. Comp.	Hardness	Crystal System	Distinguishing characteristics
1.	Pyrite	FeS_2	6.5	Isometric	Dirty yellow in reflected light. Weakly anisotropic to isotropic under crossed nicols. The polarization colours are dirty yellowish-grey. Massive in form.
2.	Pyrrhotite	Fe_{1-x}S	3.5-4.5	Hexagonal	Slightly magnetic in hand specimen. Under microscope shows strong polarization colors being anisotropic in nature. Form is massive and spindle shape laths are seen in the polished section.
3.	Marcasite	FeS_2	6-6.5	Orthorhombic	White-pale yellow in reflected light. Strongly anisotropic. Polarization colours are strong shades of blue, green, pink and violet. Tabular to needle shaped in outline. Few crystals show internal reflection.
4.	Sphalerite	ZnS	3.5	Isometric	Pale-yellow to brown in reflected light. Complex crystals showing botryoidal and colloidal bands. Isotropic in nature.
5.	Galena	PbS	2.5	Isometric	Blue-white-grey in colour. Octahedral to subparallel in outline. Distinct cleavage and triangular pits are seen. Isotropic in nature.
6.	Calcite	CaCO_3	3	Trigonal	Massive to tabular in form. White-grey in colour. At places yellowish brown in colour, probably due to iron content. Anisotropic under crossed nicols. Twinning and cleavage is distinct.
7.	Dolomite	$\text{CaMg}(\text{CO}_3)_2$	3.5-4	Trigonal	Same as calcite but more fine-grained. Distinct zoning is seen occasionally. Cleavage is distinct.

characteristics on which textural interpretation is based.

*indicates polished section
+indicates thin section

S. No.	Sample No	Texture	Description
1.	P 29*	---	The presence of sphalerite, galena and dolomite is observed in this polished section. It is interpreted that sphalerite replaces dolomite and in turn is replaced by galena. The galena crystals are euhedral to subhedral in outline and their contact with sphalerite is distinct. Distinct cleavage is seen in the case of galena. Dolomite inclusions are present throughout the sphalerite mass.
		<u>Colloform Texture:-</u>	Well developed colloform texture is represented by this section. The light and dark coloured bands of sphalerite are arranged in alternate fashion. At places, cavity filling nature is also marked. (Fig. 1, Plate II).
2.	P 29+	<u>Combined Crustified-Ring texture:-</u>	Delicate crustification of sphalerite mass is noticed here. Galena crystals are pyramidal and cubic in outline and are embedded in sphalerite mass. A few of them are sitting right on the top of light coloured sphalerite bands while succeeding dark bands of sphalerite enveloped the galena crystals and curvature of its upper surface seems to be controlled in part by the shape of the galena crystals. Similar texture was described by Bastin (1950) in zinc ore from Aachen, Germany. (Fig. 2, Plate II).
		<u>Rosette Texture:-</u>	Presence of rounded, pollen like aggregate of sphalerite indicates rosette texture. Several of these rosettes are clustered, but a few of them are separate and distinct in outline. Within rosette, dark and light coloured sphalerite bands are noticed. Schwartz (1951) described this texture. (Fig. 3, Plate II).
		<u>Atoll or Core Texture:-</u>	Schwartz (1951) and Edwards (1947) described this texture for the arrangement where a second mineral occurs inside an area of another. In this case galena crystal is enclosed in sphalerite mass. The outline of this arrangement is nearly spherical. Bastin (1950) described this texture as tubercle texture but probably implied a far more complex arrangement of ore minerals in calcite gangue. (Fig. 4, Plate II).

3. N-42-C/1* --- Sphalerite, galena and dolomite occur in this section. Replacement of dolomite along the rhombohedral cleavage planes by sphalerite (Fig. 5, Plate II) is seen. The following textures are interpreted in this case.
- Crustification Texture:- The texture is similar to P 29 as described previously. Sphalerite crystals are almost parallel to each other and emerge in perpendicular fashion from sphalerite bands. An open space is left in the center. The phenomenon of cavity filling has been observed. Also crustified bands have scalloped or colloform textures (Bastin, 1950). This texture is indicative of rhythmic precipitation which took place in colloidal state and suggests that colloform banding may have been caused by the fractional rhythmic crystallization. (Fig. 6, Plate II).
- Comb Structure:- Light, coloured sphalerite crystals are present in the wall of the cavity. Their long axis is perpendicular to the base of the band. The texture indicates that ore deposition took place in open space, i.e. vugs and cavities, fractures, (Fig. 7, Plate II).
- Dendritic Texture:- Galena needles are well oriented in sphalerite mass showing fine dendritic texture. The texture is indicative of the replacement of the sphalerite by galena.
4. N-42-C/1+ --- Replacement of dolomite by sphalerite along the cleavage planes is well represented by this thin section. Triangular pits are present along the cleavage plane in galena crystals.
- Dendritic Texture:- Similar to its polished section but more distinct here. (Fig. 8, Plate II).
- Cavity Filling Texture:- The phenomenon of cavity filling is well exemplified in this section. Crustified bands of sphalerite are seen. Sphalerite and galena is filling the cavities and vugs present in dolomite. (Fig. 1, Plate III).
5. N-42-C/2+ --- Presence of sphalerite, dolomite and calcite is observed in this case. The cavities and open space present in dolomite and calcite seems to have been filled by migrating sulfide solutions.
- Cavity Filling Texture:- Excellent explanation of cavity filling phenomenon in this section. The irregular concave boundaries

of dolomite indicate that it was replaced by sphalerite in part and the existing cavities were filled by the sulfide solution. In this section, the parallel arrangement of sphalerite mass indicates a possibility that dolomite and calcite was fractured along the weak planes due to minor deformation and thus the space created was filled later on by the precipitation of sulfide solutions.

- | | | | |
|-----|-----------|-----|--|
| 6. | N-42-C/2* | --- | Similar to its thin section. |
| 7. | N-42-C/3* | --- | Pyrite, marcasite, sphalerite and dolomite are present in this section. Well developed crystals of sphalerite are seen filling dolomite cavities. Numerous dolomite inclusions are present in pyrite-marcasite-sphalerite mass. The pyrite and marcasite mass is fine grained and is in sharp contact with sphalerite. Minor scale zoning is seen in the case of sphalerite. (Fig. 2, Plate III). |
| 8. | N-42-C/3+ | --- | The section shows contact of pyrite-marcasite mass with sphalerite and calcite. The calcite crystals are rhombohedral and are replaced by sphalerite along the cleavage planes. Calcite shows lamellar twinning. (Fig. 3 and 4, Plate III). |
| 9. | N-42-C/4* | --- | This section also indicates the presence of pyrite-marcasite, sphalerite and dolomite. Pyrite shows zonal texture. Pyrite and marcasite are intergrown. The sphalerite is in contact with pyrite and dolomite. The relationship of sphalerite with that of dolomite indicates that sphalerite is replacing dolomite. The relationship with pyrite is not very clear and it is not certain whether pyrite replaces sphalerite or not. |
| 10. | N-42-C/4+ | --- | The presence of calcite, and pyrite is observed here. Pyrite seems replacing calcite. Calcite shows good cleavage and forms veins in pyrite mass. Calcite crystals are embedded in pyrite mass and show defined boundaries. |
| 11. | N-42-C/5* | --- | Galena, sphalerite and dolomite crystals are present in this section. Galena seems replacing dolomite and in turn is replaced by sphalerite. Following textures are interpreted. |

Mutual
Boundary
Texture:-

Galena, sphalerite and dolomite have their mutual boundaries. (Fig. 5, Plate III).

Core or atoll
Texture:-

Well oriented galena crystals are enclosed by successive layers of sphalerite. Sphalerite bands are

light brown to dark brown in colour. It seems that the curvature of these bands is controlled by the shape of the enclosed galena crystal. Schwartz (1951) described this texture as core or atoll texture. (Fig. 6, Plate III).

Spheroidal
or Pellet
Texture:-

There are also a few circular light coloured sphalerite discs which are enveloped by dark coloured sphalerite band and dolomite rim. In other instance a galena crystal is enveloped by the successive rims of dolomite and sphalerite. (Fig. 7, Plate III).

Zonal
Texture:-

The sphalerite crystals show zoning phenomenon. Light and dark zones of sphalerite are clearly seen. (Fig. 8, Plate III).

Colloidal
Texture:-

Sphalerite bands show colloidal texture. The description is more or less the same as given previously for the sulfides from Pine Point ore field.

12. N-42-C/5+ ---

This thin section shows multiple twinning in case of galena crystals. Following textures are interpreted.

Pellet
Texture:-

Tiny spheroids of sphalerite, mostly homogeneous in nature, are present in dolomite matrix. At places they look same as concentric texture. The term pellet texture was proposed by Bastin in 1950. It seems that these sphalerite pellets were deposited in colloidal stage as many shrinkage cracks are present in adjoining area. Therefore a colloidal origin is much favoured in this case.

Metacolloidal
or Crackled
Texture:-

In few sphalerite pellets minute cracks are present which seem to have developed by shrinkage during crystallization of the original colloidal solution. Schwartz (1951) gave metacolloidal or crackled term for this texture. Bastin proposed the term shrinkage texture for the similar arrangement (1950). (Fig. 1, Plate IV).

13. N-42-C-3* ---

The presence of galena and sphalerite as ore minerals and dolomite as gangue mineral is observed in this ore section. The galena crystals are full of triangular pits which are filled with either sphalerite or dolomite. It seems that galena is replacing sphalerite in this case. Several sphalerite blebs are present in galena crystals. Dolomite is fine grained and light brown in colour. This brown colour

of dolomite is due to probable iron contents derived from sphalerite. Galena also replaces dolomite along its rhombohedral cleavage planes. Colloform bands are seen. (Figs. 2 and 3, Plate IV).

14. N-42-C-3+ ---

Description of minerals and its characteristics are more or less same. Their arrangement is also similar except at few places. The following textures are interpreted.

Colloform
Texture:-

The bands of light and dark coloured sphalerite are common. Where galena is present in contact with sphalerite, their relationship is clear. Needles of galena are seen in sphalerite mass. There is alternate arrangement of light and dark coloured sphalerite bands. (Fig. 4, Plate IV).

Dendritic
Texture:-

Similar to many other cases as described previously. Vanderveen used pseudodendritic textures for such arrangements formed due to replacement rather than as free growth. The needles of galena seem to replace sphalerite in this case. (Fig. 5, Plate IV).

Boxwork
Texture:-

Sphalerite aggregate shows boxwork texture in this section. Several plates and septa intersect sphalerite mass forming a box like arrangement as a secondary texture. (Fig. 6, Plate IV).

15. N-42-C-4* ---

The study of this section indicates presence of dolomite and sphalerite. Colloidal texture is represented by sphalerite bands. Most of the dolomite is replaced by sphalerite.

16. N-42-C-4+ ---

An aggregate of sphalerite, pyrite, dolomite and calcite is seen in this section. Sphalerite and dolomite inclusions are present in pyrite matrix.

Starlike
Texture:-

Wike (1960) used the term radiolith structure for this texture. (Card index of ore microphotographs-plate No. 0057). This section shows minute pyrite triplets embedded in dolomite-calcite gangue. No crystallographic orientation of pyrite triplets with respect to neighbouring gangue is inferred. Since pyrite triplets are minute star shaped without definite orientation, "Starlike Texture" seems a more appropriate description. Pyrite stars are simply at random accumulation of spoke like triplets. Several such triplets are intergrown to form random clusters.

17. O-42-C-1(A)* --- The presence of marcasite, sphalerite, galena and dolomite is observed in this case. Marcasite crystals are tabular, lath shaped, euhedral to subhedral in shape and their orientation seems to have been controlled by crystallographic directions of sphalerite matrix in which these marcasite crystals are embedded. The irregular concave boundaries of galena crystals indicate that galena is younger and replacing sphalerite. Several tiny inclusions of marcasite are present in dolomite.
18. O-42-C-1(A)+ --- Similar to its polished section but colloform bands of sphalerite are clearly visible.
19. O-42-C-1(B)* --- Very similar to O-42-C-1(A). Colloform banding is seen in this case.
20. O-42-C-1(C)* --- The section shows the presence of marcasite, sphalerite, galena and dolomite. The mineral arrangement in this section poses a problem to describe a suitable texture. The textural similarity with "Hypidiomorphic texture" of magmatic origin in igneous rocks is convincing in this case. The term seems to be more suitable as no other appropriate term is available for such arrangement. (Bastin, 1950).

Hypidiomorphic

Texture:-

Marcasite crystals are euhedral to subhedral in outline and are embedded in sphalerite matrix. It seems marcasite is present here as oriented intergrowths and most likely was controlled by the crystallographic directions of the sphalerite. The arrangement of marcasite and sphalerite is similar to hypidiomorphic texture of the igneous rocks. It may possibly be termed as crystallographic texture. (Schwartz, 1951; Bastin, 1950). (Fig. 7, Plate IV).

Spheroidal or Pellet

Texture:-

The small pellets or discs of sphalerite are embedded in galena crystal. The texture is very similar to concentric texture. (Fig. 8, Plate IV). Galena replaces dolomite at cleavage planes. Galena boundaries are concave and indicate that galena being younger replaces dolomite. Dolomite crystals are bladed and rhombohedral in outline. The dolomite is yellowish-white, fine grained and saccaroidal in texture. A little calcite is present.

Cavity Filling

Texture:-

Similar to previously described sections. Colloidal sulfide solution filled the cavities and open spaces. Inclusions of dolomite are abundant in sphalerite.

- | | | | |
|-----|--------------|---|---|
| 21. | O-42-C-1(C)+ | <u>Skeletal
Texture:-</u> | Delicate skeletons of galena are seen to be present in calcite mass. It seems that galena is replacing calcite along its cleavage planes. Galena skeletons also enclosed in sphalerite mass are seen in this section. A little dolomite is seen present inside the skeleton framework. |
| 22. | PP-A* | --- | The polished section indicates the presence of pyrite, pyrrhotite, marcasite and dolomite. Pyrrhotite and marcasite crystals are anisotropic. Possibly pyrrhotite precipitated first and replaced dolomite. Marcasite and pyrite seems to have been precipitated simultaneously. Following textures are interpreted in this case. |
| | | <u>Zonal
Texture:-</u> | Marcasite and dolomite crystals show zoning phenomenon. (Fig. 1, Plate V). |
| | | <u>Lamellar or
Triangular
Texture:-</u> | Lamellae of marcasite and pyrite are seen either arranged in parallel pattern or cutting each other forming triangular pattern. The shape of lamellae is spindle like laths which are embedded in dolomite matrix. The pyrite and marcasite is intergrown. Probably orientation of marcasite crystals was controlled by the crystallographic directions of gangue minerals. The pyrrhotite laths are bladed in shape. A description of such texture was given by Schwartz (1951) and Edwards (1947). (Fig. 2 and 3, Plate V). |
| 23. | PP-B* | --- | Presence of marcasite, pyrite and dolomite is observed in this case. Very much similar to PP-A. Little calcite is seen here. Marcasite-pyrite mass seems to have been precipitated simultaneously. No individually well developed crystals of marcasite are seen in this section. |
| 24. | PP-M* | --- | Sphalerite forms veins in dolomite and seems replacing it. Galena shows the presence of triangular pits along the cleavage planes. Dolomite is saccharoidal in texture. |
| 25. | WP* | --- | This polished section shows the presence of sphalerite, galena and dolomite. Almost all dolomite is replaced by the sphalerite. Well developed galena crystals are present in sphalerite mass. |
| 26. | PRM-1* | --- | The presence of pyrite, marcasite, galena sphalerite, and dolomite was observed in this sample. It seems that pyrite is replacing dolomite. The boundary relationships among galena, pyrite, and |

sphalerite are quite clear. It is apparently understood from the nature of their arrangement that galena is replacing sphalerite. Near the contact of pyrite and sphalerite several small stringers of sphalerite intruding the pyrite mass are present (Fig. 4, Plate V). The above relationship suggests that sphalerite is replacing earlier formed pyrite and dolomite. Galena shows distinct cleavage planes along which several triangular pits are developed. Galena was probably last to precipitate and is seen enclosing several globules of sphalerite (Fig. 5, Plate V). Dolomite is mostly replaced by the pyrite and is intergrown with marcasite. Only a few, small tabular marcasite crystals are present in this sample. Probably marcasite and pyrite represent a co-precipitation phase. In places dolomite is very fine-grained and seems to be recrystallized. On the basis of the above observations the following textures are interpreted.

Colloform
Texture:-

The prominent rhythmic banding suggests colloform texture an appropriate description. Here pyrite cubes are arrested by light and dark bands of sphalerite. The shape of this aggregate looks like a deflated pollen grain. The outermost band is of galena followed by the pyrite. The galena seems to be inserted in the large pyritic mass and pyrite seems to be intergrown with marcasite. Occasionally within pyrite-marcasite mass distinct marcasite crystals are seen (Fig. 6, Plate V).

Shredded
Texture:-

The irregular grains of pyrite are enclosed in sphalerite while sphalerite blebs are inserted into the pyrite mass. The relationship is clear at the contact of sphalerite and pyrite. (Fig. 7, Plate V).

27. PRM-2A*

The presence of pyrite, marcasite, galena and sphalerite was observed as ore mineral and dolomite and calcite as gangue minerals. Dolomite served as host rock for ore bearing solution. Following textures were interpreted in this case.

Mutual
Boundary
Texture:-

This is essentially an exsolution texture but also has been observed as replacement texture. In this case it is interpreted as replacement texture. The pyrite seems to be intergrown with marcasite. The marcasite-pyrite mass is replacing dolomite and calcite mass. The dolomite, pyrite, marcasite, sphalerite and galena crystals wherever seen in close contact show mutual boundary relationships (Fig. 8, Plate V). The pyrite is very fine grained

in several places. Intergrowth of marcasite and pyrite suggests a phenomenon of co-precipitation. Galena crystals are euhedral to subhedral in shape and are in contact with pyrite and sphalerite contents. A little twinning and distinct cleavage was seen in galena.

Shredded
Texture:-

Similar to PRM-1. It seems here that sphalerite is replacing pyrite and is being replaced by galena (Fig. 1, Plate 6). The sharp contact in between sphalerite and pyrite is well marked. Blebs and rosettee of sphalerite are either enclosed or inserted in the pyrite mass. This indicates the phenomenon of replacement. At places sphalerite shows inclusions of pyrite and dolomite. Near the sphalerite and pyrite contact galena is a bit distorted in form and shows several triangular pits along the cleavage planes. It seems that galena is replacing pyrite in this case. Some places texture seems to be graphic-growth in appearance. Well developed crystals of dolomite and calcite are seen in the sample. They seem to have suffered the phenomenon of recrystallization. Sphalerite shows the sharp contacts with the dolomite. In some places dolomite and calcite seem to suffer a slight shearing effect and also shows twinning. It moreover indicates that they have probably undergone a period of metamorphism prior to precipitation of the ore bearing fluids.

Colloform
Texture:-

As in the case of PRM-1.

Needle
Shaped
Texture:-

Needle like marcasite crystals are embedded in the sphalerite-dolomite matrix. It seems to be an oriented growth of marcasite in this case. (Fig. 2, Plate VI).

28. PRM-2B*

Dolomite, pyrite, and marcasite are present in this case. The textural interpretation is rather difficult in this case. On the basis of the arrangement and relationship the following textures were interpreted.

Rim
Texture:-

Here a distinct grain of dolomite is surrounded by a rim of pyrite and then followed by marcasite. In places the texture may be interpreted as net or mesh texture. Pyrite is fine-grained and envelops the dolomite crystal. Marcasite crystal has better rim and shows clear boundary relation with pyrite. (Fig. 3, Plate VI).

	<u>Zonal Texture:-</u>	The texture was initially described by Edwards (1947). In this case dolomite grains show the zoning phenomenon. Well marked twinning is also common. (Fig. 4, Plate VI).
	<u>Lamellar or Triangular Texture:-</u>	Edwards (1947) first described this texture and later on Schwartz (1951) gave the name of triangular texture where lamellae are arranged in cross cutting way. In this case lamellae of pyrite are seen in the marcasite mass. These are very thin and almost running parallel except in places where they make triangular arrangements. The term seriate texture was also given to lamellae or laths which are seen in a more or less definite pattern. (Figs. 5 and 6, Plate VI). At places dolomite shows twinning and a little zoning phenomenon. Euhedral - subhedral crystals of pyrite are present in the dolomite matrix.
29. PRM-2B+	<u>Comb Texture:-</u>	Well developed sphalerite crystals are present in the wall of the cavity. In general they point towards the center of the cavity. They also indicate cavity filling nature. Replacement of dolomite along cleavage planes by sphalerite. (Fig. 7, Plate VI).
	<u>Concentric/ Pellet Texture:-</u>	Small circular pellets of sphalerite are present in this section. The dark sphalerite is in center of the pellet and is surrounded by the light band of sphalerite. The origin for this texture is attributed to colloidal processes. At places, sphalerite shows zoning.
30. PRM-3*	---	In this sample, pyrite, marcasite and galena are present as ore minerals and dolomite and calcite as gangue minerals. The texture is more or less one of oriented intergrowth. Following types of texture is interpreted in this case.
	<u>Porphyroblastic Textue:-</u>	Not often used for ores but there is no suitable substitute (Schwartz, 1951). In this case euhedral crystals of pyrite are present in the matrix of sphalerite and dolomite (Fig. 8, Plate VI). Sphalerite grains are smaller here and form fine aggregate. Marcasite crystals are seen in contact of pyrite with undefined boundaries. Inclusions of gangue minerals are very common in the matrix.
	<u>Fracture Filling Texture:-</u>	Minor fractures are common in pyrite which are filled with either sphalerite or dolomite. The cavities are also filled by the migrating solutions as is indicated at a few places in the polished section.

Paragenesis:-

On the basis of textural interpretation and the mutual arrangement of different minerals the paragenetic sequence is interpreted. Carbonates served as host rock. The relationships among different mineral constituents is well defined except where they have a complex mutual arrangement. Only one sample indicated the presence of pyrrhotite (Fe_{1-x}S) in association with pyrite and marcasite. Sphalerite and galena are ubiquitous. Pyrite and marcasite are common and pyrrhotite is rare. The textural study made it possible to outline the paragenetic sequence for Pine Point sulfides. It is understood from their mutual arrangement that pyrrhotite was first to precipitate replacing dolomite and deposited in open spaces. Following pyrrhotite precipitation, pyrite and marcasite precipitated almost simultaneously as a co-precipitation phase. Sphalerite was next to precipitate and was followed by galena. Certain textural evidences suggest that there was an earlier phase of galena precipitation before sphalerite came into the picture.

The final paragenetic diagram is constructed from a series of such diagrams made for individual samples during the interpretation of ore textures and is set forth in Figure 8.

Discussion:-

For purpose of discussion the following two points have been considered.

1. Paragenesis and mineral distribution.
2. Causes of precipitation.

Paragenesis and mineral distribution.

The paragenetic sequence for Pine Point sulfides indicate the order of deposition as pyrrhotite, pyrite, marcasite, sphalerite, galena and calcite. Variations, overlapping and repetition are not frequent but present. Galena was seen replacing dolomite as well as sphalerite. This relationship indicates the repetition of galena.

PYRRHOTITE

PYRITE

MARCASITE

GALENA

SPHALERITE

GALENA

CALCITE

FIG. 8. Paragenetic Diagram For Pine Point Sulphides, Pine Point Ore Field, N.W.T., Canada.

In all probability the precipitation of galena took place before and after the precipitation of zinc sulfide. The veins and irregular cavities show the crustification and colloform banding that is characteristic of open space filling. Not only open space filling but evidences for replacement have been observed during the textural studies of Pine Point sulfides. The following description is an attempt to understand the paragenetic relations governing mineral distribution.

Pyrrhotite- Pyrrhotite seems to have been precipitated first among the Pine Point sulfides. The relationship to this evidence is well defined in ore sample No. PP-A. The bladed pyrrhotite laths are embedded in the dolomite matrix and were seen cut by laths of pyrite-marcasite mass. This relation suggests a younger generation for pyrite-marcasite. The replacement of pyrrhotite by pyrite-marcasite mass is also seen in the same polished section. Pyrrhotite seems to have formed by the replacement of dolomite.

Pyrite and Marcasite- Pyrite-marcasite, as the second sulfides to be deposited are found commonly with Pine Point ore. They seem to have precipitated simultaneously and hence represent a co-precipitation phase. In most cases, pyrite and marcasite were seen intimately intergrown replacing dolomite with one exception where they were seen to replace pyrrhotite. In a few ore sections it is seen that pyrite is well developed in its cube and octahedron form embedded in a dolomite matrix. Their relationship represents a great variation in textures. The marcasite crystals vary from euhedral to subhedral and massive form. Sometimes they occur in bladed to spindle shape and other times in cubes to pyramidal outline. At one place, euhedral to subhedral marcasite crystals were seen embedded in sphalerite matrix where they seem to have been controlled by crystallographic directions of sphalerite crystals.

Sphalerite- Sphalerite was next to precipitate after the deposition of iron sulfides. A sharp contact between iron sulfides and zinc sulfide was observed in many cases.

Sphalerite is one of the major constituents of the Pine Point sulfides. It is seen replacing dolomite along the cleavage planes and also filling irregular open spaces. In general it occurs as the massive form but a few well developed crystals were also observed.

Several textures were observed in case of sphalerite and they all indicate a colloidal to metacolloidal state of ore bearing solutions during the time of precipitation. It seems conditions responsible for precipitation remained unchanged for most of the time except for a little fluctuation in chemical composition which caused rhythmic colloform banding in sphalerite.

Galena - The main galena deposition followed the bulk of sphalerite deposition. Evidence also indicates an earlier precipitation of galena before the bulk deposition of sphalerite. This evidence is based on the observation of galena inclusions in massive sphalerite and also replacement of earlier formed pyrite-marcasite by galena. Galena is present almost in each sample examined from Pine Point ore field. It varies in size from tiny specks to crystals nearly 2 cm, in diameter. Similarly variations in shape from well developed cube to irregular skeleton were also observed. The cube shaped galena seems to have preference for light coloured sphalerite as it is seen in many cases that galena cubes are sitting right on the light sphalerite band succeeded by dark coloured band whose outline was controlled by the shape of galena crystals. In brief, boundary relations of both types show control by sphalerite faces, control by galena faces and mutual relations. Later formed galena shows slight overlapping. The main deposition took place in available open spaces. However evidences for replacement are not scanty.

Calcite - Calcite was probably the last mineral to deposit. It is found as veins in earlier formed minerals and in vugs. In places, thin layers of calcite were seen around sphalerite. This relationship also indicates a possibility of overlapping during deposition.

Causes of Precipitation

Paragenesis and mineral distribution suggest that uniform conditions prevailed during the course of mineral deposition. This view is supported by the presence of a similar set of minerals in each sample, their identical habits and mutual arrangement. There is also an almost uniform distribution of minor elements. This combination indicates that there was essentially no change in conditions responsible for mineral precipitation. However, apart from this similarity, the ratio of sphalerite to galena may suggest a minor scale zoning and hence there should be a spatial relation of sphalerite to galena within the Pine Point ore bodies. Having visualized these relations it could be explained that within Pine Point ore bodies the location of open spaces controlled the distribution of sphalerite and galena. Of course, such control more likely depends upon time and sequence of deposition.

Here "first come, first served" was the basis for the order of precipitation. That is to say the earlier precipitated minerals first occupied the available open space and later precipitated minerals were satisfied with still unoccupied open spaces. It is probable that the composition of mineralizing solutions might have had basic control over such open space precipitation. The paragenetic sequence of Pine Point sulfides suggests that earlier formed minerals such as pyrrhotite, pyrite and marcasite, were iron rich while later formed minerals were zinc and lead rich. This interpretation indicates a change in mineralizing solutions with time with a resurgence of iron from time to time. A slight change in composition of mineralizing solution could also have been brought about by the presence of certain minor elements which might have been derived from carbonates and shales through which these solutions were travelling.

An alternate explanation to the mineral association might be established if allowance was made for changing conditions such as temperature, pressure, sulfur activity etc., which might have been instrumental at the time of precipitation. A little support is offered from the studies on the iron contents of sphalerites, separated

from Pine Point sulfides. Whatever conditions may have existed during the precipitation of Pine Point sulfides it is almost certain that the bulk amount of galena precipitated after the deposition of sphalerite. Assuming the above discussion as valid, the causes for sulfide precipitation in Pine Point ore field now may be evaluated.

If we assume that Pine Point mineralizing solutions were essentially connate brines containing metals as chloride complexes, then chloride ions might have facilitated the transport of metals in mineralizing solutions. Since Pine Point sulfide deposits occur at a shallow depth, these mineralizing solutions have travelled at least some distance from the place where they were trapped as connate brines to the place of precipitation. This movement of mineralizing solutions must have been caused by some factor - probably igneous activity in the Cordillera (Baadsgaard, et al., 1966). Once the solutions were set in motion the possibility of reacting with wall rock and mingling with groundwater became more favourable. It is well within the limits of understanding that such mixing of ore solutions with groundwater will cause the dilution of connate brine and subsequent precipitation of sulfides. The explanation for earlier precipitation of sphalerite could be offered if the presence of neutralizing bicarbonate ions existed in groundwater and reactions with wall rock occurred (Bradbury, 1961). It is also possible that the precipitation of sphalerite took place even before the dilution of mineralizing solutions when the zinc sulfide was in colloidal to metacolloidal state.

Subsequent to precipitation of zinc sulfide, lead held in the solution with a high concentration of chloride ions precipitated as lead sulfide. The work of Newhouse (1932) and Garrels (1941) suggested that a high chloride concentration in the mineralizing solution is responsible for the late deposition of galena. Similar interpretations have recently been made by Helgeson (1964). Besides dilution, the cooling effect of groundwater is also an important factor in causing precipitation. For the purpose of sulfide precipitation such as at Pine Point, there is need of continuous supply of sulfur in some or the other form and it is proposed that in Pine Poine ore field the sulfur

was present in carbonate reservoirs before the arrival of mineralizing solution. This sulfur was derived from the direct reduction of seawater sulfates (Folinsbee et al., 1966).

CHAPTER - V

ISOTOPIC STUDIES

In 1951, Urey and his co-workers concluded that O^{18} isotope in calcium carbonate varies with the temperature at which it is deposited from water. This variation in abundance can be used as a geologic thermometer. Subsequent studies developed a palaeotemperature scale (Urey 1951, Epstein 1953). An effort to measure the variation of O^{18}/O^{16} isotopes in Pine Point carbonates was attempted in the present study and palaeotemperatures evaluations is based on the Clayton's data (1960) for higher temperature. The purpose of this study is to evaluate the temperature limits for carbonates at Pine Point as an aid to understanding the genesis of Pine Point ores.

THEORETICAL CONSIDERATIONS

O^{18}/O^{16} Isotopes and Geothermometry - Oxygen is the most abundant element of the earth's crust. Three stable isotopes of oxygen, O^{16} , O^{17} , and O^{18} having relative abundance of 99.759:0.0374:0.2039 are present in the atmosphere. The variation in O^{18}/O^{16} ratios have been found to be as much as 10%. Epstein's (1959) work indicated that lowest observed ratio was found in glacier ice near the poles while highest occurred in the atmospheric carbon dioxide. Urey (1947) presented new data on oxygen isotopes after extending the earlier calculations of Urey and Greiff (1935). They expressed the belief that the O^{18} content of $CaCO_3$ could be used as geologic thermometer. Urey's calculation showed that a change in temperature of precipitation from 0° to $25^\circ C$ should change the O^{18} content of calcite by a factor of 1.004. Later in 1951, Urey described a more refined mass spectrometric method for the comparison of two samples; it had an accuracy of 0.02% of the O^{18} content which made possible determination of the temperature of formation to $1^\circ C$.

Further improvements were made and in 1953, Epstein and Mayeda developed the following empirical isotopic scale based on several temperature controlled

experiments.

$$t^{\circ}\text{C} = 16.5 - 4.3 (\delta_c - \delta_w) + 0.14 (\delta_c - \delta_w)^2$$

where $\delta_c = \text{O}^{18}$ of the carbonate. (Standard PDB-1)

$\delta_w = \text{O}^{18}$ of the water (Standard CO_2 extracted from PDB-1 with H_3PO_4)

The equation given above indicates a direct relationship between water and precipitated carbonates in it and, therefore, isotopic composition of water and carbonate could be determined. If isotopic composition of water is known and O^{18} content of carbonate is measured, the temperature of carbonates can be calculated with the help of the paleotemperature scale. Certain assumptions are made while considering paleotemperature measurements and these may be outlined as following:-

1. The calcium carbonate deposited is in isotopic equilibrium with water.
2. The isotopic composition of the carbonate does not change after deposition.
3. The isotopic composition of oxygen in ocean water has not changed during the time span considered.

Fractionation Factor-

The available information indicates that most of the stable isotope fractionation in nature is the result of exchange reactions occurring at or near equilibrium. For example water vapour over oceanic water is in equilibrium (Epstein and Mayeda, 1953)., CaCO_3 deposited by some marine organisms has an $\text{O}^{18}/\text{O}^{16}$ ratio determined by the equilibrium fractionation between CaCO_3 and H_2O (Epstein, et al., 1953); minerals in hydrothermal veins are often crystallized in equilibrium with one another and with the fluid phase from which they have been precipitated (Clayton, et al., 1958).

Fractionation is by far the most important factor in measuring the various isotopic exchange equilibrium constants (K) over a wide range of temperature. Such measurements were made significantly in one geologic system; $\text{CaCO}_3 - \text{H}_2\text{O}$.

The fractionation factor is designated by α and is defined as the overall ratio of the isotopes of an element in one chemical compound as compared with the same ratio in a second chemical compound (Epstein, 1959)

$$\alpha_c = \frac{R_{\text{CO}_3}}{R_{\text{H}_2\text{O}}}, \quad R = \text{O}^{18}/\text{O}^{16}$$

Since equilibrium constant is equal to fractionation factor, the following exchange reaction establishes the relationship with that of K_c and consequently α_c .

Isotopic Exchange Reaction

K_c = Equilibrium constant for carbonate.

α_c = Fractionation factor for carbonate.



$$K_c = \frac{(\text{O}^{18}/\text{O}^{16})_{\text{CaCO}_3}}{(\text{O}^{18}/\text{O}^{16})_{\text{H}_2\text{O}}}$$

$$K_c = \alpha_c$$

(McCrea, 1950 and others).

Epstein and his co-workers measured the variations in $\text{O}^{18}/\text{O}^{16}$ ratios of calcite deposited by marine organisms. Their data is in a range of $+7^\circ$ to $+30^\circ\text{C}$ and is in close accordance with the results obtained by McCrea (1950). High temperature measurements were made by Clayton (1959) who recrystallized calcite in a high pressure apparatus in the temperature range 190° to 750°C . Wyllie and Tuttle (1960) expressed the belief that 750°C is the upper limit of the stability of calcite in water.

From his studies Clayton (1961) concluded that the equilibrium constant at 25°C for isotopic exchange between carbonate and water is 1.02855 and an empirical equation which fits the experimental data over the temperature range of

0°-750°C, is;

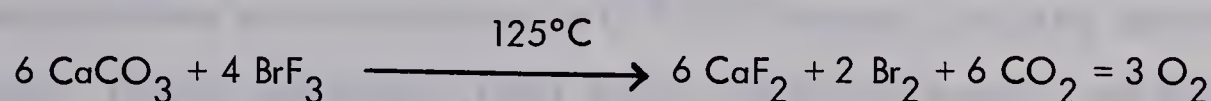
$$\ln k = 2730 \, T^{-2} - 0.00256$$

K = Equilibrium-Constant

Clayton and Epstein (1958) determined the value α_a ($\alpha_a = \frac{R_{CO_2}}{R_{CO_3}}$)

as 1.01000 but later on (1961) they found that the previous α_a value was not in agreement with new α_a value. Clayton was successful in extracting total oxygen and this could be shown by following reaction. (For detailed information, reference to Clayton's papers on oxygen isotope fractionation which appeared in 1961, may be made).

Reaction -



Many carbonates react to completion in a few hours but normally yield 2/3 of the total oxygen of the carbonate as carbon dioxide. (This factor depends on the stoichiometry of the reaction). In this reaction there is fractionation of oxygen isotopes and it is most essential to consider the α_a ($\alpha_a = \frac{R_{CO_2}}{R_{CO_3}}$) factor while measuring $\text{O}^{18}/\text{O}^{16}$ ratios. It was earlier thought that the isotopic fractionation in the phosphoric acid reaction is the same from one carbonate to another but Sharma and Clayton (1965) showed that this assumption is not true. Sharma and Clayton (1965) have measured the α_a value for several alkaline earth and transition metal carbonates and showed that the determination of oxygen isotopes abundances in carbonates involve a large kinetic isotope effect while extracting CO_2 from carbonates for isotopic analysis of oxygen and carbon. This CO_2 is liberated on the decomposition of the carbonates with 100% phosphoric acid at 25°C.

Their researches led to conclusion that there are significant differences in the isotopic fractionation factors associated with the phosphoric acid procedure for CO_2 liberation from various carbonates. This difference is significant in case of dolomite and calcite. Fractionation factors for calcite and dolomite are as given below:

$$\alpha_{\text{a Cal.}} = 1.01008$$

$$\alpha_{\text{a Dol.}} = 1.01090$$

O¹⁸/O¹⁶ Ratios in Coexisting Dolomite and Calcite

The fractionation of oxygen isotopes between coexisting dolomite and calcite has not been firmly established but generally it has been accepted that a relatively large fractionation of O¹⁸/O¹⁶ exists and that the difference in δO^{18} values ($\Delta\text{dol.-cal.}$) in a coexisting pair is temperature dependent. Studies performed by Engel, Clayton and Epstein (1958) on Leadville limestone of Mississippian age indicated that there is no fractionation of O¹⁸/O¹⁶ between coexisting dolomite and quartz. Clayton and Epstein (1958), Engel, Clayton and Epstein, and Epstein (1959) found a range of Δ quartz-calcite of 1.9 to 7.4 permil and concluded that the higher the Δ value, the lower the estimated temperature of the formation. They suggested that the Δ of coexisting dolomite-calcite pairs as well as quartz-calcite pairs could be used to estimate temperatures of the formation since there is no fractionation between quartz and dolomite.

Friedman and Hall (1963) found a little fractionation of O¹⁸/O¹⁶ between coexisting dolomite and calcite during the study of low temperature Mississippi Valley type lead-zinc deposits. The dolomite-calcite pairs are more abundant in these deposits rather than dolomite-quartz pairs. However, no apparent fractionation was found between coarse dolomite crystals in vugs and veins enclosing fine grained dolomite crystals in vugs and veins and veins enclosing fine grained dolomite. (Friedman and Hall, 1963). On the contrary, Engel, Clayton and Epstein (1958) found a large fractionation of O¹⁸/O¹⁶ between calcite and coarse white dolomite (both from high temperature environment). The studies of Friedman and Hall (1963) on calcite-dolomite pairs suggested almost no fractionation between calcite and coarse white dolomite (both from high temperature environment). The studies of Friedman and Hall (1963) on calcite-dolomite pairs suggested almost

no fractionation between calcite and dolomite and they concluded that "no fractionation was found either in an unaltered interbedded limestone and dolomite section or in fine intergrowths of calcite-dolomite in hydrothermal alteration zones around lead-zinc orebodies in southern Wisconsin. Fine grained dolomite and coarsely crystalline dolomite filling vugs and fractures from four different districts of Mississippi Valley type deposits have about the same δO^{18} as opposed to the large fractionation found at Leadville".

From their studies of coexisting calcite and dolomite pairs of recent and ancient sediments, Degens and Epstein (1964) concluded that the δO^{18} of the dolomite is the same or greater than that of the coexisting calcite but the carbon isotope values of the measured carbonates are usually within the range found for marine limestone. Previous data on the $\text{O}^{18}/\text{O}^{16}$ ratios indicate that at equilibrium the dolomite value should be greater by about 8 permil at room temperature relative to that of calcite (Clayton, and Epstein, 1958, Engel et al. 1958). Epstein's (1963) result supported this interpretation (Epstein et al., 1963). Degens and Epstein (1964) expressed the view that in the light of the considerable isotope fractionation between calcite and dolomites, it may be expected that the dolomites and calcites precipitated in the same environment of deposition will also have a difference in δ -value of about 6-10 per mil at room temperature. Recently Schwarcz (1966) found from his studies on coexisting metamorphic calcites and dolomites that the oxygen-isotope fractionations decrease erratically with increasing metamorphic grade up to the garnet zone but rocks of higher grade (kyanite-sillimanite zone) were found to be disturbed isotopically. The carbon isotope fractionation does not correlate clearly with metamorphic grade but seems to decrease with increasing temperature (Schwarcz, 1966).

Carbon Isotopes and Relative Abundance-

The two most important stable carbon isotopes are C^{13} and C^{12} . CO_2 is the

most convenient gas to use for isotopic analysis because of the fact of the relatively large differences in the masses of C^{13}/C^{12} , easy handling in mass spectrometer and wide distribution of carbon in nature. The abundance of C^{13} and C^{12} in carbonates as determined by Nier is as follows:

$$C^{13} - 1.108\%$$

$$C^{12} - 98.892\%$$

In nature, there is pronounced variation in isotopic constitution of carbon and such variation could be measured by considering C^{13}/C^{12} ratios. Many experimental results indicate that the heavier isotope C^{13} tends to concentrate in carbonates and the lighter C^{12} in organic matter.

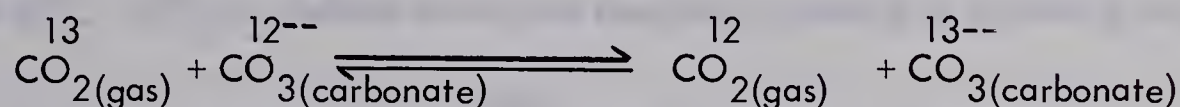
Generally carbonates show a range of isotopic composition greater than that of any other group except graphites, the range of δ being about 24‰. This variation of C^{13}/C^{12} ratios in carbonates may be ascribed to the following probable factors;

1. That organism considerably affect the C^{13}/C^{12} ratios in the carbonates.
2. That variation may be caused by the process of photosynthesis.
3. Possible equilibration occurs with carbon dioxide derived organically.
4. That the degree of attainment of isotopic equilibrium during precipitation may vary.

McCrea (1950) was successful in calculating the fractionation of O^{18} and C^{13} between carbonate ions in calcite lattice and in aqueous solution. His calculations indicate that C^{13} should be enriched in solid calcite by 4.2 per mil at $0^{\circ}C$, and 3.8‰ at $25^{\circ}C$. Craig (1953) analyzed the organic carbon from marine sources to determine the isotopic composition of living marine organisms. This indicates that the organic carbon is high in C^{12} and marine plants contain more C^{13} than land plants. Craig's values for atmospheric carbon dioxide indicate a lower content of C^{12} than those previously reported. He considers that CO_2 collected near cities may have varying proportions of carbon derived from burning coal, wood, oil, etc.

and suggests the use of CO_2 collected from the air over the oceans to reduce the chance of contamination. Ingerson (1953) indicates that the graphite from the Canyon Diablo meteorite is approximately 11% heavier than carbon of iron carbide of the same sample. He suggested that this fact should be taken into consideration while measuring and interpreting the $\text{C}^{13}/\text{C}^{12}$ ratios of meteorites.

The experimental results of McCrea (1950) and Baertschi (1957) emphasize the significance of the following exchange reaction:



The fractionation factor for this exchange reaction is as follows:

$$\alpha_{\text{CO}_2} = \frac{\text{C}^{13}/\text{C}^{12}_{\text{CaCO}_3}}{\text{C}^{13}/\text{C}^{12}_{\text{CO}_2}} \cong 1.01 \text{ at } 26^\circ\text{C}$$

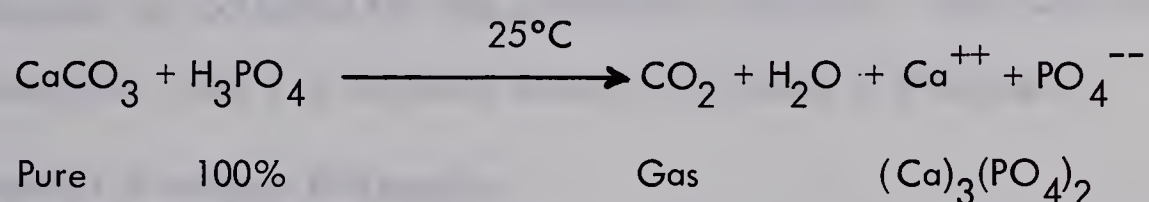
This means that CO_3^{--} (carbonate) is about 10 per mil richer in C^{13} than corresponding CO_2 .

EXPERIMENTAL PROCEDURES

Selection of Material— The carbonate samples used in this study were obtained from Pine Point drill cores and ores (see Figs. 10 and 13 and Table 11). All samples were thoroughly cleaned, examined and ground with the help of agate mortar before the analyses. Thin sections were prepared for all such samples and were stained with Alizarin-S to examine calcite and dolomite petrographically. In several cases, dolomite was separated from the carbonate rock by attacking it with the dilute acetic acid. To insure the purity of these samples, each one of them was checked by x-ray diffraction and it was found that they are well within the acceptable limits of purity.

Preparation of Carbon dioxide — All carbonate samples free from detectable contamination were ground to the powder form (about 200 mesh). Powder from each sample weighing 30–50 mgr. was placed in a vessel for reaction with phosphoric acid.

The reaction vessels containing dry carbonate samples and 100% phosphoric acid were connected to a vacuum system of the extraction plant for complete degassing of the samples and acid before mixing. When required vacuum was obtained, all reaction vessels were transferred to a thermostatically regulated water tank whose temperature was kept constant at 25°C and within a short period after mixings the reaction between carbonate samples and phosphoric acid (100%, McCrea, 1950) was made to yield CO₂. Calcite was reacted for 2-3 days and dolomite from 10-15 days at 25°C. CO₂ is yielded during the reaction according to following equation.



On completion of the reaction, the reaction vessels containing carbon dioxide were connected to an extraction train to remove the CO₂ gas. During the extraction process the CO₂ was first purified by freezing down with liquid nitrogen and pumping away the uncondensed gas. Then water vapour was fixed in a dry ice and acetone bath. Finally CO₂ was frozen down with liquid nitrogen after insuring no contaminate of any kind was left either in the CO₂ itself or in the extraction plant. This carbon dioxide gas was collected in breakseals for each sample for mass spectrometric analysis.

Many samples did not directly permit a physical separation of the dolomite from the calcite or vice-versa. Therefore, a chemical technique used by Epstein et al. (1963) was applied to collect the CO₂, developed from calcite and dolomite, separately. This method takes advantage of the marked difference in the relative rates of the reaction (Table 12) of dolomite and calcite when reacted with phosphoric acid. It is now established by experimental determinations and further calculations that during one hour of fractionated reaction dolomite will yield only very little CO₂ while calcite will yield more than 90% of its CO₂. This method is a

convenient one for the separate collection of CO_2 developed from dolomite-calcite pairs reacting with 100% phosphoric acid at 25°C (see Figure 9); and holds if 50:50 ratio of dolomite and calcite is present in the sample. After one hour reaction calcite - CO_2 was collected. The gas formed between 1-6 hours was pumped away. Finally, after more than 6 hours of reaction, dolomite- CO_2 was collected.

A convenient standard, Fisher-Chemical Company reagent grade CaCO_3 , was used to obtain the reference CO_2 gas to compare the isotopic variation in oxygen and carbon. The carbon dioxide, extracted in this manner from the carbonate samples and standards was collected for mass spectrometric analyses. Data were corrected and reported vs. PDB-1 of National Bureau of Standards in Washington.

Measurement of Isotopic Differences

The instrument used in this investigation is a double collecting mass spectrometer having 90° , 12" radius magnetic analyzer. Slits were set up for simultaneous collection of ion currents of required masses for carbon and oxygen analysis. Ion current measurement and amplification was done with the help of two vibrating reed electrometers. A five-figure integrating digital voltmeter-ratiometer was used to record the ratios of output voltages from the two vibrating reed electrometers. The ratio of the two voltages, which were in turn proportional to the required masses ion current ratios, were recorded on a five-figure digital printer.

Carbon dioxide was analysed for carbon and oxygen isotopes by installing CO_2 containing breakseals on the sample-manifold system. After obtaining a suitable vacuum for sample line for analysis, an aliquot of sample and standard was introduced into the respective mercury reservoirs. The CO_2 pressure behind the capillary leaks was adjusted by raising the mercury level until both the sample and standard line produced the same ion current on the single collection of the 44 beam. Measurements of the required masses for carbon and oxygen analysis were printed by five-figure digital printer. In each case, 10 values of the ratio

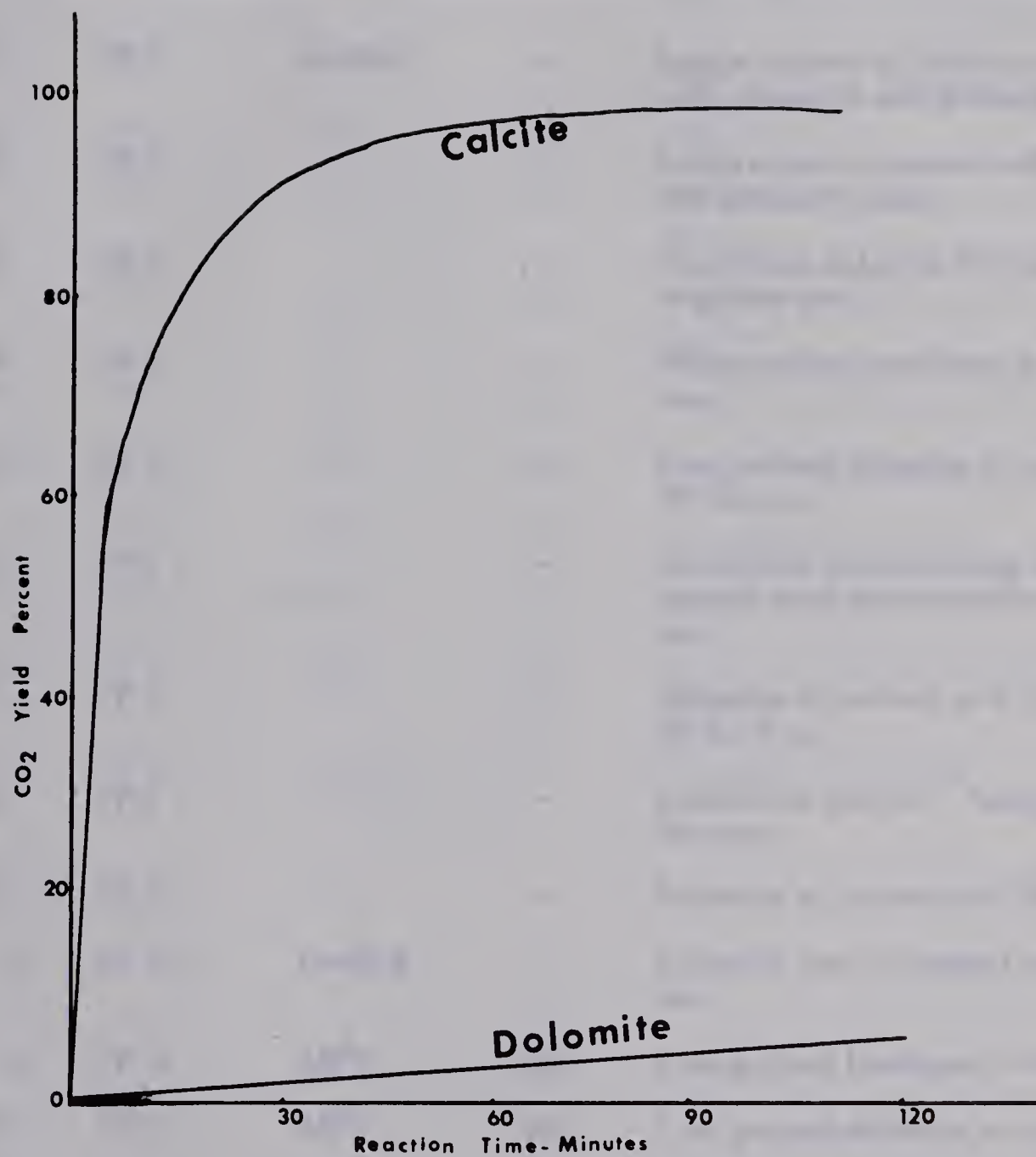


Fig. 9. Fractionated reaction time and corresponding CO₂ yield from calcite-dolomite pair.

(After Epstein et al. 1964)

Table 11: Samples record and their lithology.

S. No.	Sample No.	Source No.	Core Depth (in feet)	Description
1.	PP 1	N-42-C	-	Single crystals of calcite associated with sphalerite and dolomite.
2.	PP 2	"	-	Calcite vein in contact with galena and sphalerite ores.
3.	PP 3	"	-	Crystalline dolomite filling large vugs in galena ore.
4.	PP 4	"	-	White calcite associated with Pb-Zn ore.
5.	PP 5	"	-	Fine grained dolomite in contact with Pb-Zn ore.
6.	PP 6	"	-	Crystalline calcite filling vugs and in contact with pyrite-sphalerite-galena ore.
7.	PP 7	"	-	Dolomite in contact with limestone and Pb-Zn ore.
8.	PP 8	"	-	Crystalline calcite. Associated with the ore.
12.	PP 12	"	-	Dolomite in contact with Pb-Zn ore.
13.	PP 13	N-42-R	-	Dolomite vein in contact with Pb-Zn ore.
14.	PP 14	BH#3	334	Fine grained limestone in vugs.
15.	PP 15	BH#3	360	Fine grained dolomite in vugs.
17.	PP 17	BH#4	311	Fine grained dolomitic limestone.
18.	PP 18	BH#4	393	Hydrothermal dolomite with traces of calcite and bitumen.
19.	PP 19	BH#4	448	Reef dolomite, fine grained with traces of bitumen.
21.	PP 21	BH#1	309	Dolomite with traces of bitumen.

22.	PP 22	BH#1	396	Dolomite associated with calcite and bitumen.
24.	PP 24	BH#2	411	Dolomite with traces of limestone, sulfur and bitumen. Also white veined dolomite is present.
25.	PP 25	BH#8	175	Dolomite with calcite veins.
26.	PP 26	BH#5	262	Limestone.
27.	PP 27	BH#5	271	White veined dolomite with trace calcite.
28.	PP 28	BH#5	365	White veined dolomite with trace calcite.
29.	PP 29	BH#7	340	Hydrothermal dolomite from vugs.
30.	PP 30	BH#7	373	White veined dolomite.
31.	PP 31	BH#7	400	Fine grained dolomite.
32.	PP 32	BH#6	291	Crystalline dolomite.
33.	PP 33	BH#6	337	Dolomite with traces of bitumen and clay.
34.	PP 34	N-42-R	-	Fossiliferous limestone.

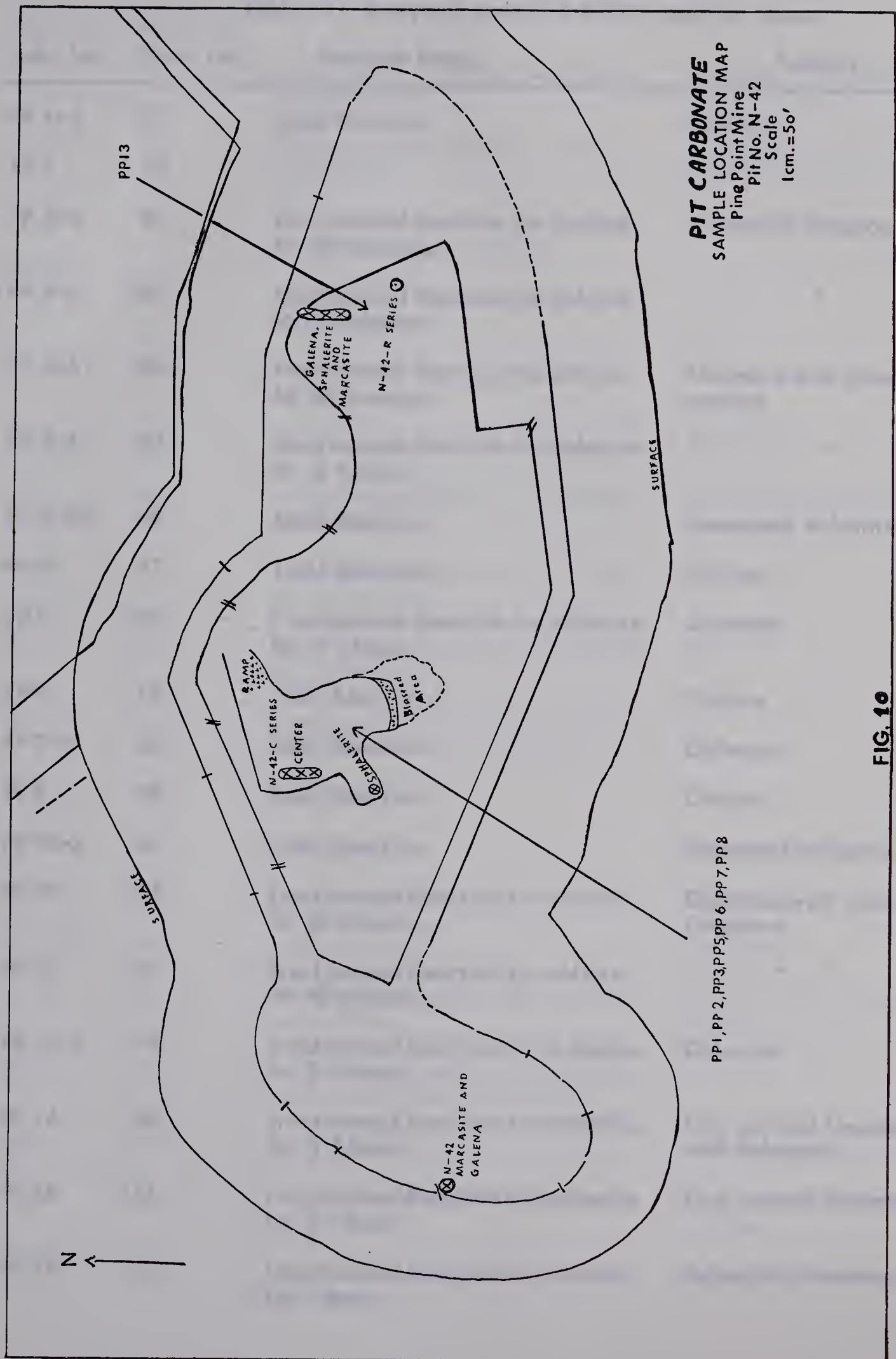


FIG. 10

Table 12: Analyzed samples and their reaction range.

Lab. No.	Prep. No.	Reaction Range	Remarks
PP 1-A	27	Total Reaction	Calcite
PP 2	18	" "	"
PP 3-A	96	Fractionated Reaction for calcite for 45 minutes.	Dolomitic limestone
PP 3-A	103	Fractionated Reaction for calcite for 35 minutes.	" "
PP 3-A1	88	Fractionated Reaction for calcite for 45 minutes .	Dolomite with trace calcite
PP 3-A1	93	Fractionated Reaction for dolomite for > 4 hours.	" " " "
PP 3-A2	40	Total Reaction	Separated dolomite
PP 4	17	Total Reaction	Calcite
PP 5	160	Fractionated Reaction for dolomite for > 1 hour.	Dolomite
PP 6	19	Total Reaction	Calcite
PP 7-4	53	Total Reaction	Dolomite
PP 8	28	Total Reaction	Calcite
PP 12-2	43	Total Reaction	Separated dolomite
PP 13	104	Fractionated Reaction for calcite for 45 minutes.	Dolomite with trace limestone
PP 13	97	Fractionated Reaction for calcite for 45 minutes.	" " " "
PP 13-1	94	Fractionated Reaction for dolomite for > 4 hours.	Dolomite
PP 14	90	Fractionated Reaction for dolomite for > 4 hours.	Fine grained limestone with dolomite
PP 15	161	Fractionated Reaction for dolomite for > 1 hour.	Fine grained dolomite
PP 17	173	Fractionated Reaction for calcite for 1 hour.	Dolomitic limestone

Table 12...continued

PP 17	78	Fractionated Reaction for dolomite for > 6 hours.	Dolomitic limestone
PP 18	68	Fractionated Reaction for calcite for one hour.	Hydrothermal dolomite with trace calcite
PP 18	75	Fractionated Reaction for dolomite for > 6 hours, 15 minutes.	" " " " "
PP 18	98	Fractionated Reaction for calcite for 45 minutes.	" " " " "
PP 18	105	Fractionated Reaction for calcite for 35 minutes.	" " " " "
PP 19	140	Total Reaction	Dolomite
PP 21	95	Fractionated Reaction for dolomite for > 4 hours.	Dolomite with trace calcite.
PP 21	99	Fractionated Reaction for calcite for 45 minutes.	" " " "
PP 21	106	Fractionated Reaction for calcite for 35 minutes.	" " " "
PP 22	76	Fractionated Reaction for dolomite for > 6 hours and 15 minutes.	" " " "
PP 24-A	50	Total Reaction	Dolomite
PP 25-A	49	Total Reaction	Dolomite
PP 25-B	137	Total Reaction	Dolomite
PP 26-B	115	Total Reaction	Limestone
PP 27	70	Fractionated Reaction for calcite for one hour.	Dolomite with trace calcite.
PP 27	77	Fractionated reaction for dolomite for > 6 hours and 15 minutes.	" " " "
PP 27	157	Total Reaction	Separated dolomite
PP 28	163	Fractionated Reaction for dolomite for > 1 hour.	Dolomite with trace calcite.
PP 29	164	Fractionated Reaction for dolomite for > 1 hour.	Hydrothermal dolomite

Table 12...continued

PP 30	165	Fractionated Reaction for dolomite for > 1 hour.	Hydrothermal dolomite (white veins)
PP 31	166	Fractionated Reaction for dolomite for > 1 hour.	Dolomite
PP 32	139	Total Reaction	Dolomite
PP 33	159	Total Reaction	Dolomite
PP 34	59	Total Reaction	Limestone

were recorded for the sample and standard. To insure the reproducibility of the results a fair amount of repetition was done. The data are reported as per mil deviation defined as:

$$\delta_{C^{13}} = \left[\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] \times 1000$$

Where:

$R_{\text{sample}} = C^{13}/C^{12}$ ratio in the sample.

$R_{\text{standard}} = C^{13}/C^{12}$ ratio in the standard.

$\delta_{O^{18}}$ is defined in similar terms of O^{18}/O^{16} ratios. Appropriate correction factors as described by Craig (1957) were applied. A precision of ± 0.1 per mil was obtained for the mass spectrometric analysis. Overall error is $\sim \pm 0.2\%$.

CORRECTION FACTORS

Certain correction factors must be applied to mass spectrometric analysis as suggested by Craig (1957). In case of carbon analysis, the masses 44 and 45 are collected simultaneously and the ratio is expressed as following:

$$R_{45} = \frac{C^{13}O^{16}O^{16} + C^{12}O^{16}O^{17}}{C^{12}O^{16}O^{16}}$$

where:

$$R_{45} = \frac{\text{Number of mass 45 ions collected}}{\text{Number of mass 44 ions collected}}$$

The final expression of this correction factor was derived by Craig (1957) for the C^{13} analysis as following:

$$\delta_{C^{13}} = \left[\frac{R_{45}(\text{Std})}{R_{13}(\text{Std})} \right] - \left[\frac{R_{17}(\text{Std})}{2R_{13}(\text{Std})} \right] \delta_{O^{18}}$$

where:

δ_m = Measured enrichment obtained from the recorded ratio of the molecular mass.

δ_c = True enrichment of the sample ratio to standard.

$$R13 = C^{13}/C^{12}$$

$$R17 = O^{16}O^{17}/O^{16}O^{16}$$

O^{16} = corrected oxygen enrichment

The substitution of above ratio terms in the equation by numerical values will give following final product.

$$C^{13} = 1.0674 \delta_m - 0.0336 \delta_{O^{18}}$$

(This equation is valid for our working standard only)

(For derivation of the equation and final product readers may refer to Craig's paper on "Isotopic standards for carbon and oxygen" published in 1957).

Similarly for the analysis of oxygen, the measurement of mass 46 ion beam vs. combined mass 44+mass 45 ion beam is made. The following ratio in terms of isotopic molecules was given by Craig (1957);

$$R46 = \left[\frac{C^{12}O^{16}O^{18} + C^{13}O^{16}O^{17} + C^{12}O^{17}O^{17}}{C^{12}O^{16}O^{16} + C^{13}O^{16}O^{16} + C^{12}O^{16}O^{17}} \right]$$

But the desired ratio is following;

$$R18 = \left[\frac{C^{12}O^{16}O^{18} + C^{13}O^{16}O^{18}}{C^{12}O^{16}O^{16} + C^{13}O^{16}O^{16}} \right] = \left[\frac{C^{12}O^{16}O^{18}}{C^{12}O^{16}O^{16}} \right]$$

On the basis of further derivations and calculations a final equation was derived by Craig (1957) and only the final expressions are reproduced here.

$$1 + \delta_m = \frac{\left[1 + \delta_c + \frac{(1 + \delta_c^{13})R13(Std)(1 + \frac{\delta_c}{2})R17(Std)}{R18(Std)} \right]}{\left[1 + \frac{R13(Std)R17(Std)}{R18(Std)} \right]}$$

Where all other expressions in the equation are same as given previously except for -

$$R_{18} = \frac{O^{16}}{O^{18}} / \frac{O^{16}}{O^{16}}$$

$$R_{46} = \frac{\text{Number of mass 46 ions collected}}{\text{Number of mass 44+mass 45 ions collected}}$$

By substituting ratio terms with numerical values, we arrived at following correction factor for oxygen analysis.

$$\delta_{cO^{18}} = 1.0013 \delta_m + 0.009 \delta_{cC^{13}}$$

(The above correction factor was derived against our working standard).

Since in our laboratory the working standard is different from that of PDB standard, a further correction as suggested by Cheney and Jensen (1965) is required and this may be expressed by following equation;

$$\delta_{xs} = \delta_{xw} \left(1 + \frac{\delta_{ws}}{1000} \right) + \delta_{ws}$$

Where:

δ_{xs} = Per mil value of the sample with respect to commonly accepted standard (PDB).

δ_{xw} = Per mil value of the sample with respect to working standard
(in our case Fisher's Lab. Reagent - $CaCO_3$).

δ_{ws} = Per mil value of working standard with respect to the commonly accepted standard.

For purpose of absolute accuracy, above correction factors should be applied to mass spectrometric analyses.

Results and Discussion:

The δ -values of analyzed carbonates are presented in the Table 13-15 and Figures 11 - 15. The data indicate different generations of dolomite and calcite samples. For convenience the following points are considered for results and discussion.

Carbon isotopic composition versus oxygen isotopic composition of carbonates from the Pit No. N-42, Pine Point Mine, N.W.T.

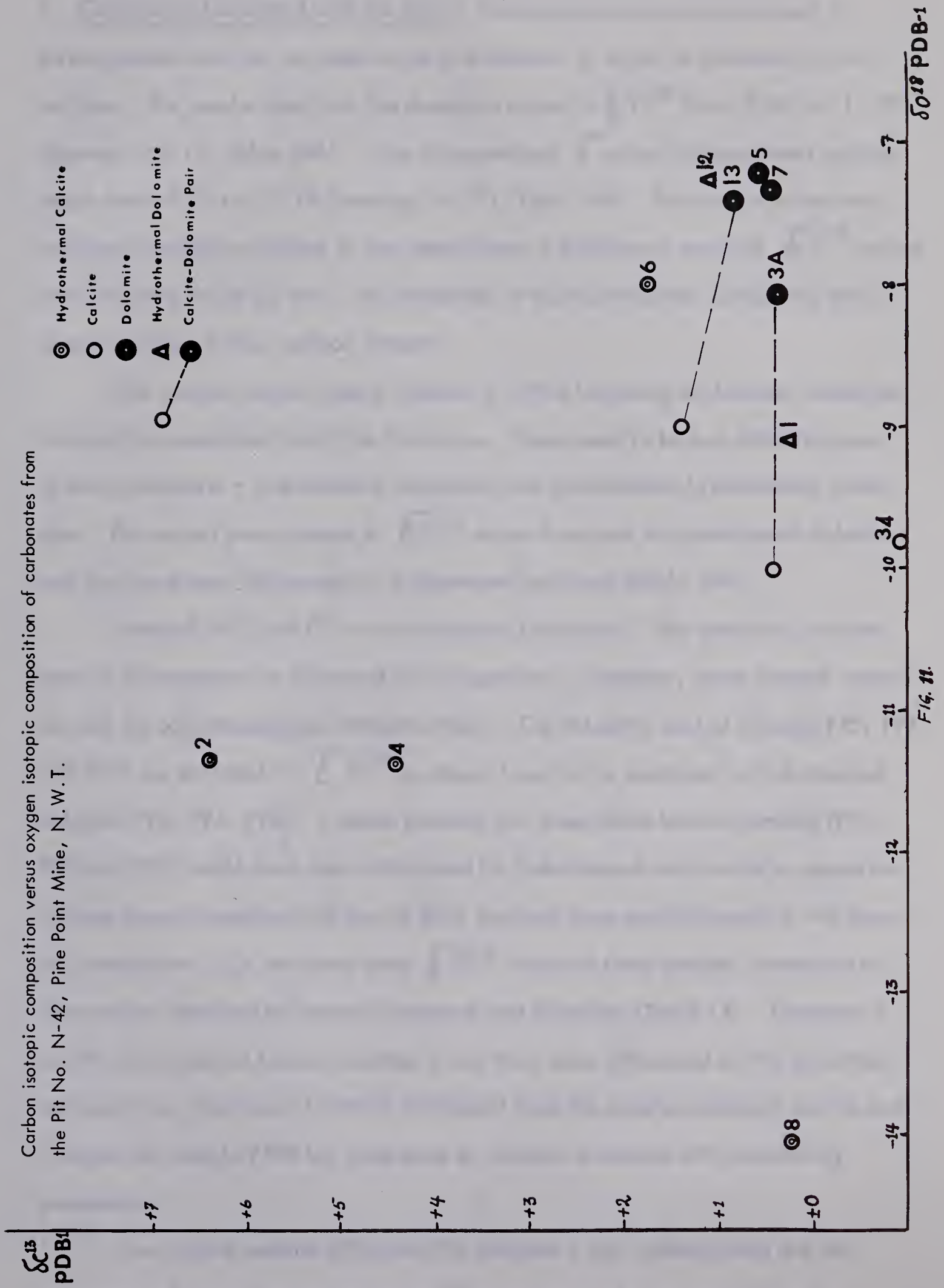


Fig. 11.

1. Carbonates Associated with the Ore - The dolomites and calcites present in direct contact with the ore seem to be hydrothermal in origin as indicated by thin sections. The results show that the dolomites range in δO^{18} from -9.08 to -11.70 (average -10.17, Table 14A). The corresponding δ values for associated calcites range from -8.01 to -15.05 (average -12.70, Table 14B). The carbon values are consistent throughout except in two cases where it indicates a range of δC^{13} values from +4.25 to +6.38 per mil. The remainder of the hydrothermal carbonates show a minor variation in their carbon content.

The oxygen isotope results indicate a 2-5‰ fractionation between dolomites and calcites associated with Pine Point ores. There seem to be two definite groups of such carbonates - hydrothermal carbonates and intermediate hydrothermal carbonates. The second group ranges in δO^{18} values from reef to hydrothermal dolomites and may have been influenced by hydrothermal solutions (Table 14A).

Samples PP13 and PP3-A are dolomitic limestones. The coexisting calcites seem to be secondary as indicated by thin sections. Therefore, these samples cannot be used for paleotemperature determinations. The dolomitic part of Samples PP5, PP7 and PP13 are enriched in δO^{18} by about 4 per mil as compared to hydrothermal calcites (PP2, PP4, PP8). It seems possible that these three breccia samples (PP5, PP7 and PP13) might have been influenced by hydrothermal solutions as a comparison of these breccia samples with that of PP12 does not show any difference in the isotopic composition. On the other hand δO^{18} values of these samples correspond to those values obtained for marine limestones and dolomites (Table 14). Therefore it is difficult to decide for sure whether or not they were influenced by the hydrothermal solutions. The value for PP34 is different from the samples discussed earlier and it seems that sample PP34 has undergone an isotopic exchange with circulating groundwater.

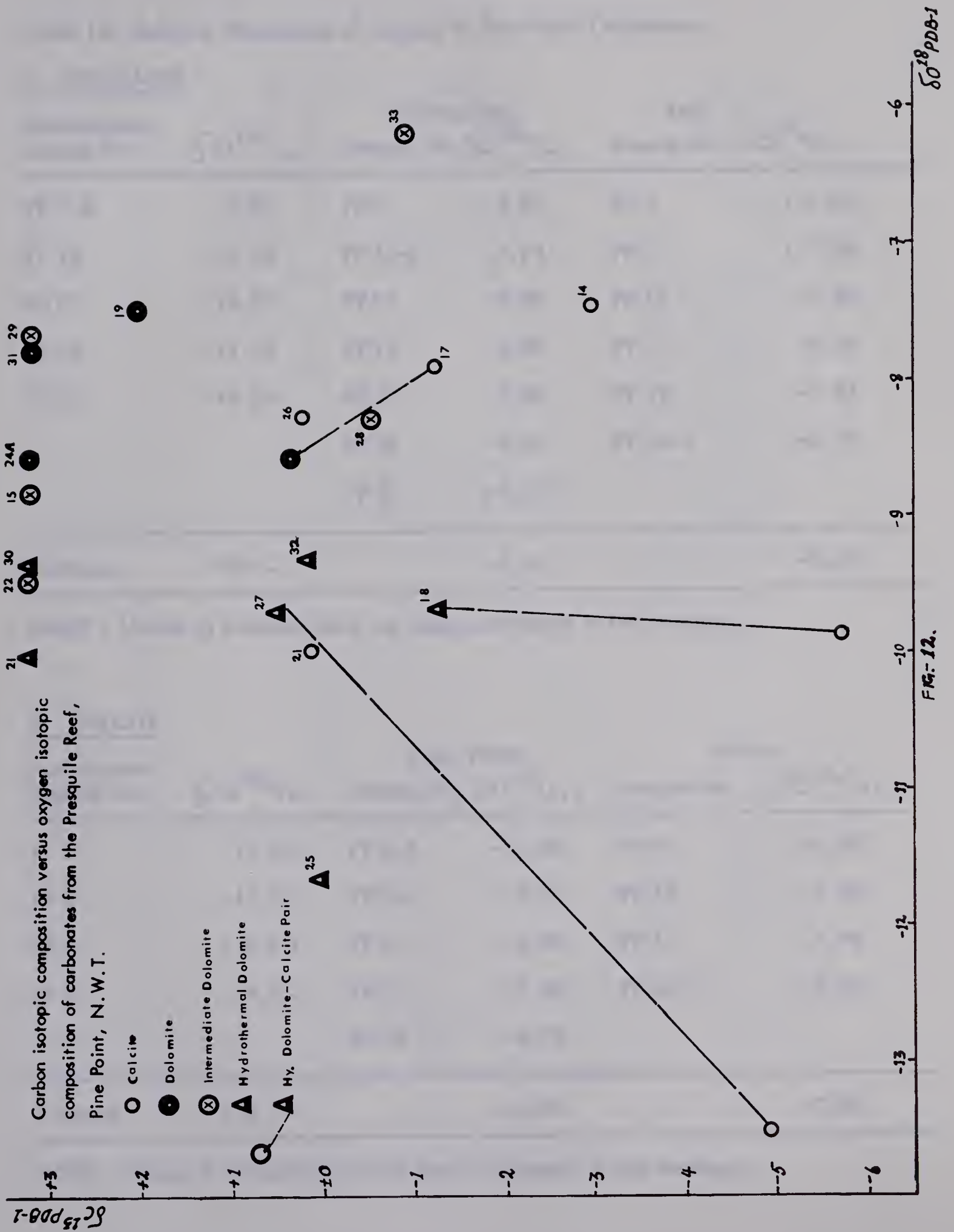
Two calcite samples (PP2 and PP4) indicate a high carbon value and this enrichment of carbon can be explained if we assume that either equilibrium in

Table 13: Isotopic composition of oxygen and carbon in carbonates from Pine Point area, N.W.T. Canada

Sample No.	Preparation No.	Sample Reference		Dolomite		Calcite		Dolomite	
		Analysis No.	Calcite	$\delta^{18}\text{O}$ (per mil)		$\delta^{13}\text{C}$ (per mil)		$\delta^{18}\text{O}$ (per mil)	
#PP 1-A	27	-	-	156/155	-	-	-	-9.08	+0.23
# PP 2	18	153/154	-	-	-11.35	+6.38	-	-	-
#PP 3-A	103,96,93,40	76/77,90/91	40/39	-	-10.00	+0.45	-	-8.03	+0.40
#PP 4	17	172/171	60/59	-	-11.39	+4.25	-	-	-
#PP 5	160	-	75/159	-	-	-	-	-7.20	+0.56
#PP 6	19	125/124	-	-	-8.01	+1.81	-	-	-
#PP 7-A	53	-	161/162	-	-	-	-	-7.30	+0.40
#PP 8	28	157/158	-	-	-14.05	+0.19	-	-	-
#PP 12-2	43	-	179/180	-	-	-	-	-7.24	+1.01
#PP 13	94,104,97	57/58,93/92	149/150	-	-9.00	+1.40	-	-7.43	+0.94
#PP 14	90	24/23	-	-	-7.55	-2.90	-	-	-
#PP 15	161	-	70	-	-	-	-	-8.90	-
#PP 17	173,78	141/142	49/48	-	-7.94	-1.21	-	-8.60	-0.45
#PP 18	75,105,68,98	79/80,89/88 94/95	36/35	-	-9.9	-5.7	-	-9.70	-1.22

Table 13...continued

# PP 19	140	-	126/127	-	-	-7.53	+2.14
# PP 21	99, 106, 95	86/87, 97/96	83	-10.0	+0.4	-10.2	-
# PP 22	76	-	66	-	-	-9.5	-
# PP 24-A	50	-	112	-	-	-8.7	-
# PP 25-A	49	-	78	-	-	-10.3	-
# PP 25-B	137	-	129/128	-	-	-11.67	-0.06
# PP 26-B	115	148/147	-	-8.03	-0.76	-	-
# PP 27	157, 70, 77	64/63	21/22, 103	-13.5	-4.9	-10.2	-0.58
# PP 28	163	-	61/62	-	-	-8.3	-0.5
# PP 29	164	-	104	-	-	-7.8	-
# PP 30	165	-	71	-	-	-9.4	-
# PP 31	166	-	115	-	-	-7.75	-
# PP 32	139	-	134/135	-	-	-9.3	+0.23
# PP 33	159	-	25/26	-	-	-6.2	-0.9
# PP 34	59	164/163	-	-9.8	-1.98	-	-



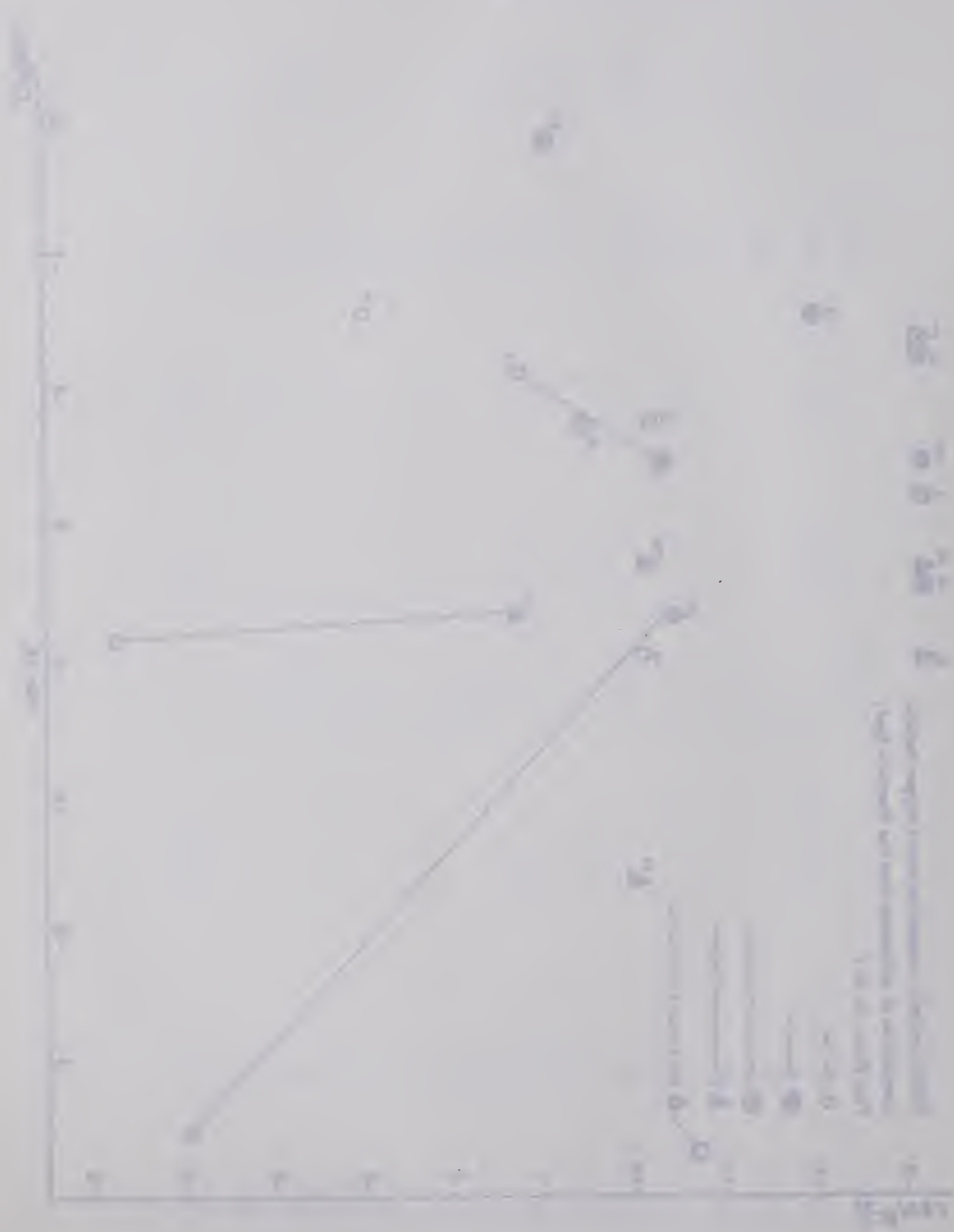


Table 14: Relative Abundance of oxygen in Pine Point Carbonates.

A. DOLOMITE

Hydrothermal Sample No.	$\delta O^{18}\text{‰}$	Intermediate Sample No.	$\delta O^{18}\text{‰}$	Reef Sample No.	$\delta O^{18}\text{‰}$
PP 1-A	-9.08	PP 3	-8.03	PP 5	(-7.20)
PP 18	-9.70	PP 12-2	-7.24	PP 7	(-7.30)
PP 21	-10.20	PP 22	-9.50	PP 13	(-7.40)
PP 25	-11.70	PP 28	-8.30	PP 17	-8.60
PP 27	-10.20	PP 29	-7.80	PP 19	-7.50
		PP 32	-9.30	PP 24-A	-8.70
		PP 33	(-6.20)		
Average	-10.17		-8.58		-8.26

NOTE - Values in brackets have not been considered in the averages.

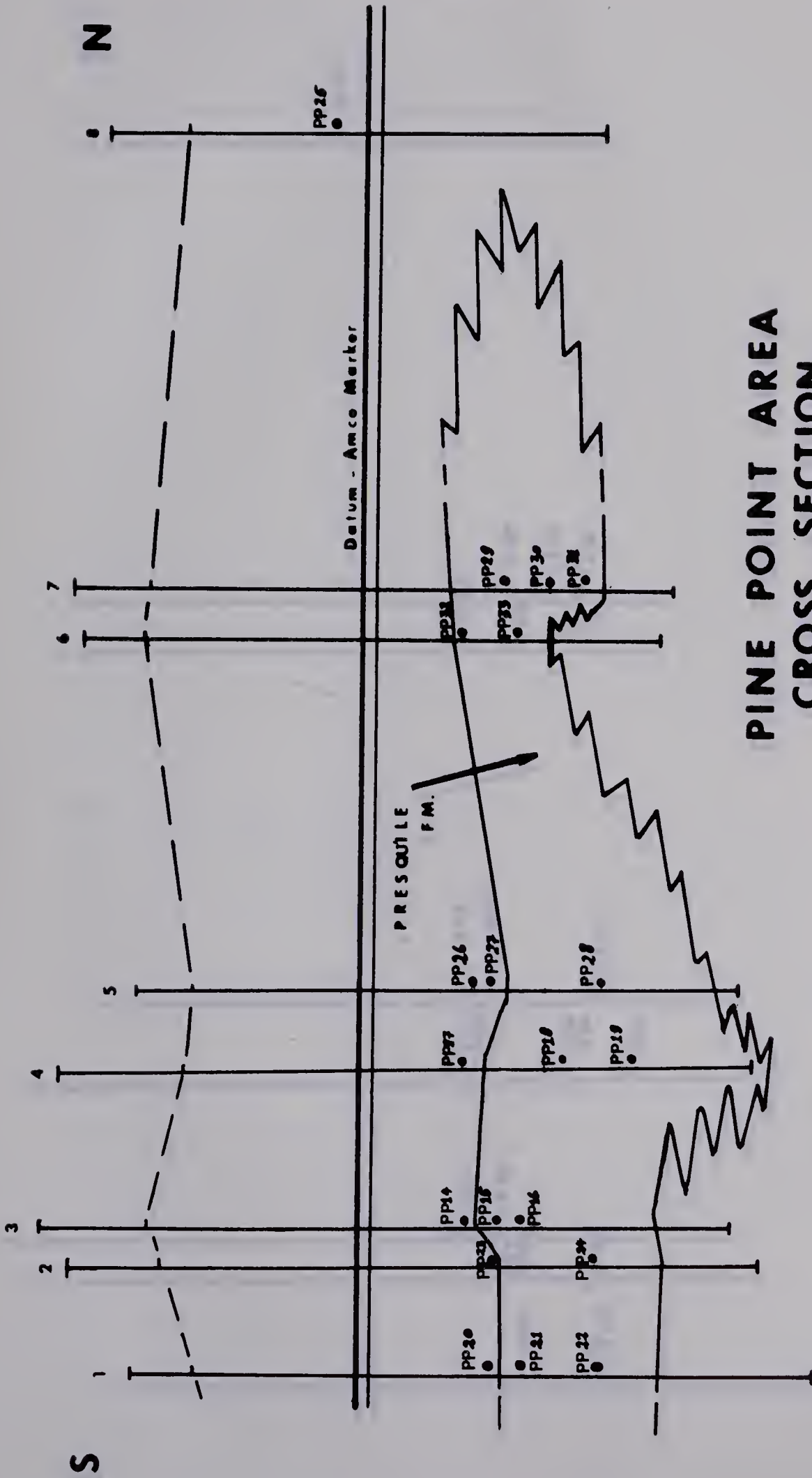
B. CALCITE

Hydrothermal Sample No.	$\delta O^{18}\text{‰}$	Fresh Water Sample No.	$\delta O^{18}\text{‰}$	Marine Sample No.	$\delta O^{18}\text{‰}$
PP 2	-11.35	PP 3-A	-10.00	PP 13	(-9.00)
PP 4	-11.39	PP 18	-9.90	PP 14	-7.50
PP 6	(-8.01)	PP 21	-10.00	PP 17	-7.94
PP 8	-14.05	PP 27	-13.50	PP 26-B	-8.03
		PP 34	-9.70		
Average	-12.70		-10.85		-7.82

NOTE - Values in brackets have not been considered in the averages.

Table 15: Relative Abundance of Carbon in Pine Point Carbonates

Sample No.	Calcite δC^{13} -PDB	Dolomite δC^{13} - PDB
PP 1-A	-	+0.23
PP 2	+6.38	-
PP 3-A	+0.45	+0.40
PP 4	+4.25	
PP 5	-	+0.56
PP 6	+1.80	-
PP 7	-	+0.40
PP 8	+0.19	-
PP 12-2	-	+1.01
PP 13	+1.14	+0.90
PP 14	-2.90	-
PP 17	-1.20	-0.45
PP 18	-5.70	-1.20
PP 19	-	-2.10
PP 21	+0.40	-
PP 25-B	-	-0.06
PP 26-B	-0.76	-
PP 27	-4.90	-0.58
PP 28	-	-0.50
PP 32	-	+0.23
PP 33	-	-0.90
PP 34	-1.98	-
Average	-0.59	-0.23



Scale: horiz.- 1 in.= 4000 ft.

vert. " 1 in.= 100 ft.

● = sample location

PINE POINT AREA CROSS SECTION SHOWING BORE HOLES AND RESPECTIVE SAMPLE LOCATIONS

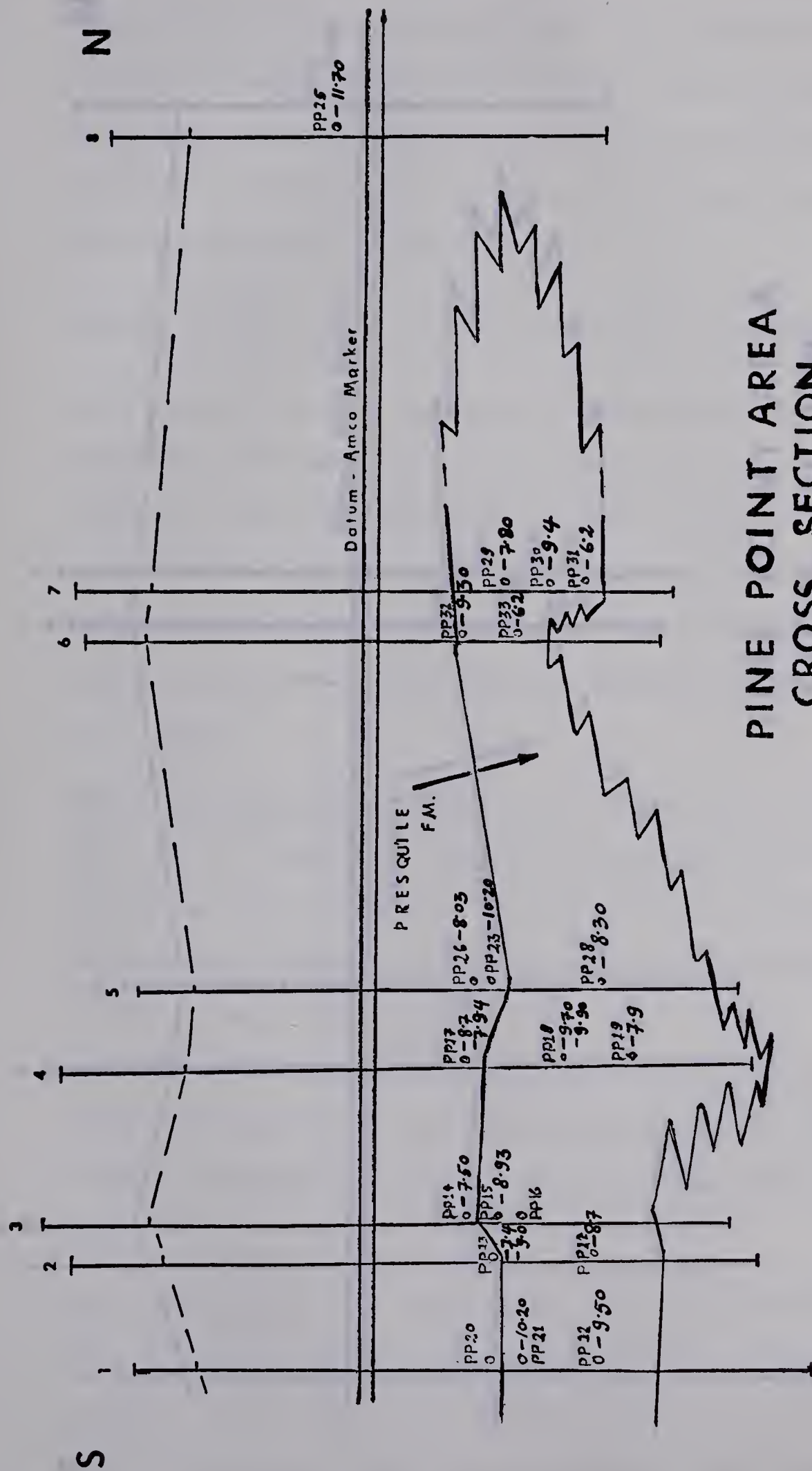
STATIONING: 100+00 TO 100+50

DATE: 10/10/10

PROJECT: 100+00 TO 100+50

NAME: JOHN V. VEE





PINE POINT AREA CROSS SECTION AND 50' SPREAD.

Scale: horiz. - 1 in. = 4000 ft.
vert. - 1 in. = 100 ft.

○ = sample location

FIG. 14

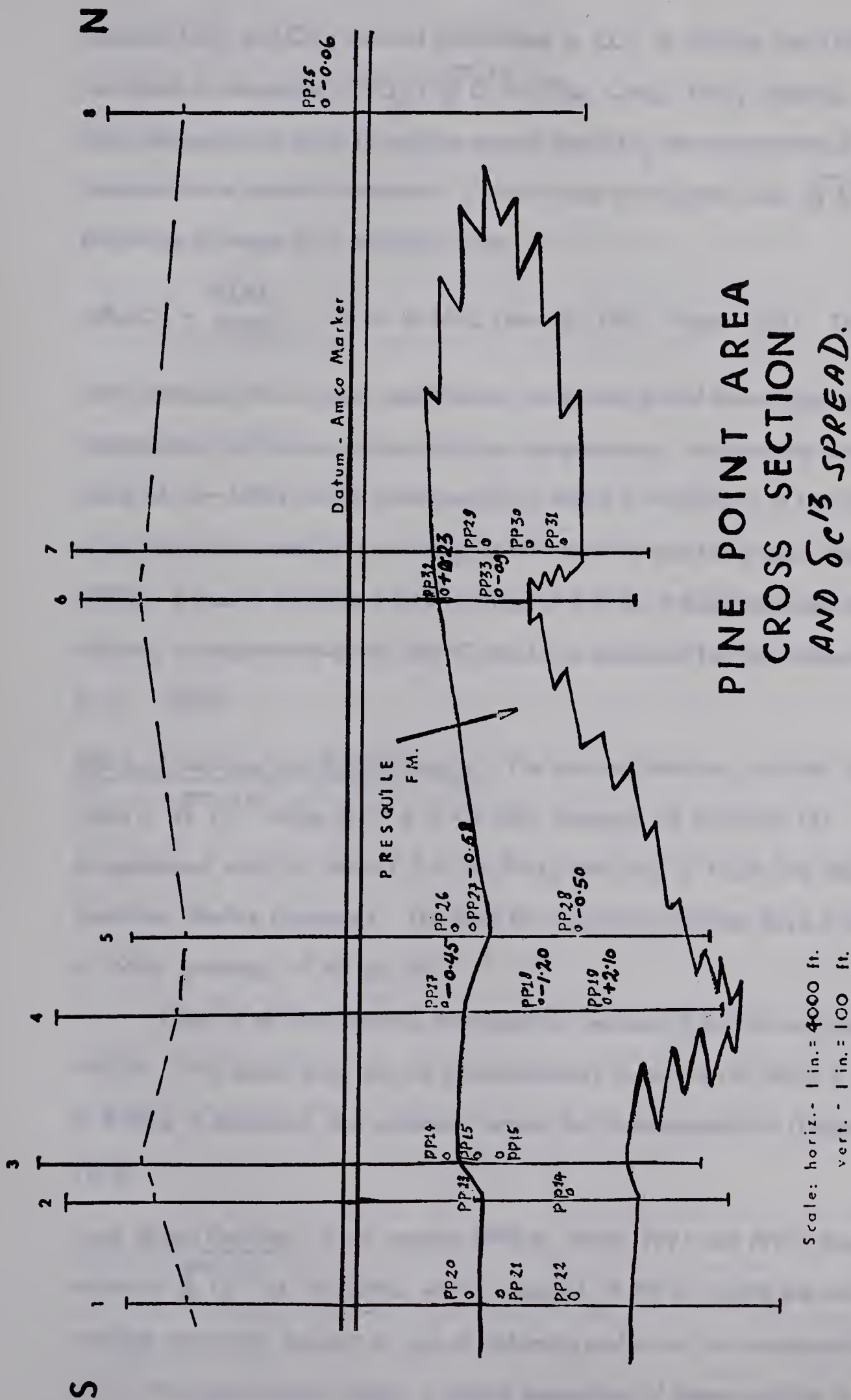


FIG-15.

between CO_2 and CO_3 was not established or CO_2 in solution was rich in δC^{13} as compared to atmospheric CO_2 ($\delta\text{C}^{13} \sim -7\text{‰}$, Craig, 1953, Keeling, 1961). This later assumption is valid if we also accept that CO_2 was produced due to thermal decomposition of marine limestone. If this is true in this case then δC^{13} of this CO_2 should be in range of -1 to 2‰ where

$$\alpha_{\text{CO}_2} = \frac{R_{\text{CO}_3}}{R_{\text{CO}_2}} = 1.01 \text{ at } 26^\circ\text{C} \text{ (Bertschi 1957, Vogel 1961)]. Therefore the}$$

newly formed calcite under equilibrium conditions should have higher values at lower temperatures and lower values at higher temperatures. As given by Craig (1953) a value of $\sim +4\text{‰}$ should be expected at 400°K ($\sim 125^\circ\text{C}$). If this is true then under favorable conditions our samples PP2 and PP4 may have been deposited below 100°C . Since in our case a fractionation of $2\text{--}5\text{‰}$ is found between dolomite and calcite, a temperature below 100°C should be expected for their deposition (Engel et al., 1958).

Marine Limestone and Reef Dolomite - The marine limestone and reef dolomites indicate a δO^{18} range of -7.2 to -8.7‰ (average -8.26 , Table 14). This value is in agreement with the value (-5 to -8.5‰) obtained by Keith and Weber (1964) for Devonian Marine Limestone. The data for coexisting calcites have a range of -7.50 to -9‰ (average -7.82 per mil).

There is no considerable fractionation between dolomite and coexisting calcite. This means they are not syngenetic in nature for which a difference of $4\text{--}8\text{‰}$ is expected, but probably formed due to metasomatism (Degens, et al., 1964).

Fresh Water Calcites - Four samples (PP3-A, PP18, PP21 and PP27) show an average value of δO^{18} as -10.25‰ with a range of -9.90 to -13.50 per mil. These calcites are mostly present in vugs of dolomite and since the corresponding dolomites fall in the hydrothermal range, a second generation of these calcites is expected.

These calcites are believed to have been deposited by circulating groundwaters as indicated by C^{13} values lighter in carbon.

Equilibrium Pairs and Paleotemperatures - Assuming that the mineral pairs used in this study were in isotopic equilibrium with their surroundings three coexisting dolomite-calcite pairs were analyzed with intention of obtaining information on temperature of formation (Table 16). The O^{18}/O^{16} data for the samples which presumably formed in the presence of adequate water are plotted in figures 16A and B. In this case Δ dolomite-calcite is a measure of temperature and δ dolomite is dependent on temperature as well as isotopic composition of water in whose presence the equilibrium was established. Clayton and Epstein (1958) estimated the isotopic composition of Leadville water experimentally and found an average value of +2‰. Since at very high temperatures ($>750^{\circ}C$) no isotopic fractionation is possible between various chemical species, temperature measurement beyond this limit will be doubtful.

The variation in the δ water values for each sample is approximately the deviation of the δ dolomite value of each point from the curve (Figure 16A). If we assume that dolomite, calcite and associated waters of the samples PP1, PP2, PP4, PP8 and PP12 were in isotopic equilibrium during the formation of minerals and if we accept Engel's original solid curve (Figure 16A) as correct, then our estimated values i.e. +3.5, +4, and -3.5 for water are correct. Considering these values as satisfactory the $[\Sigma = (\alpha - 1) \times 1000]$, (Σ = Enrichment factor) were calculated for each equilibrium pair respectively and were plotted against the "equilibrium constants versus temperature curve" of Clayton (1961) (Fig. 16B) to obtain the paleotemperatures of these pairs. Results are presented in table No. 16.

In this case the lighter δO^{18} values indicate that this depletion in oxygen is probably caused by isotopic exchange of the limestone with connate waters. The calculated Δ D-C values in the present case are small. This raises the possibility that carbonates in question have undergone certain changes. (Similar conclusions

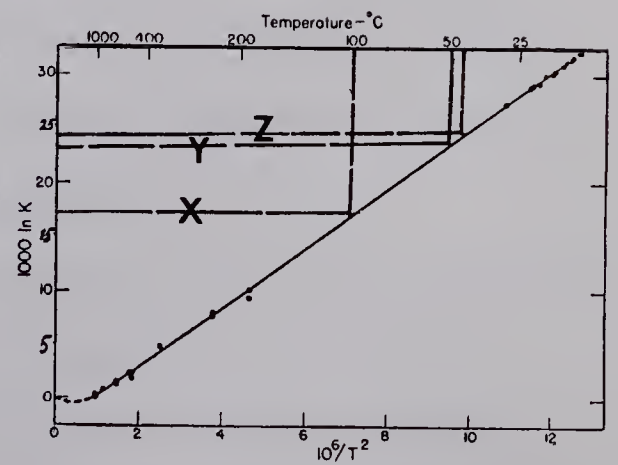
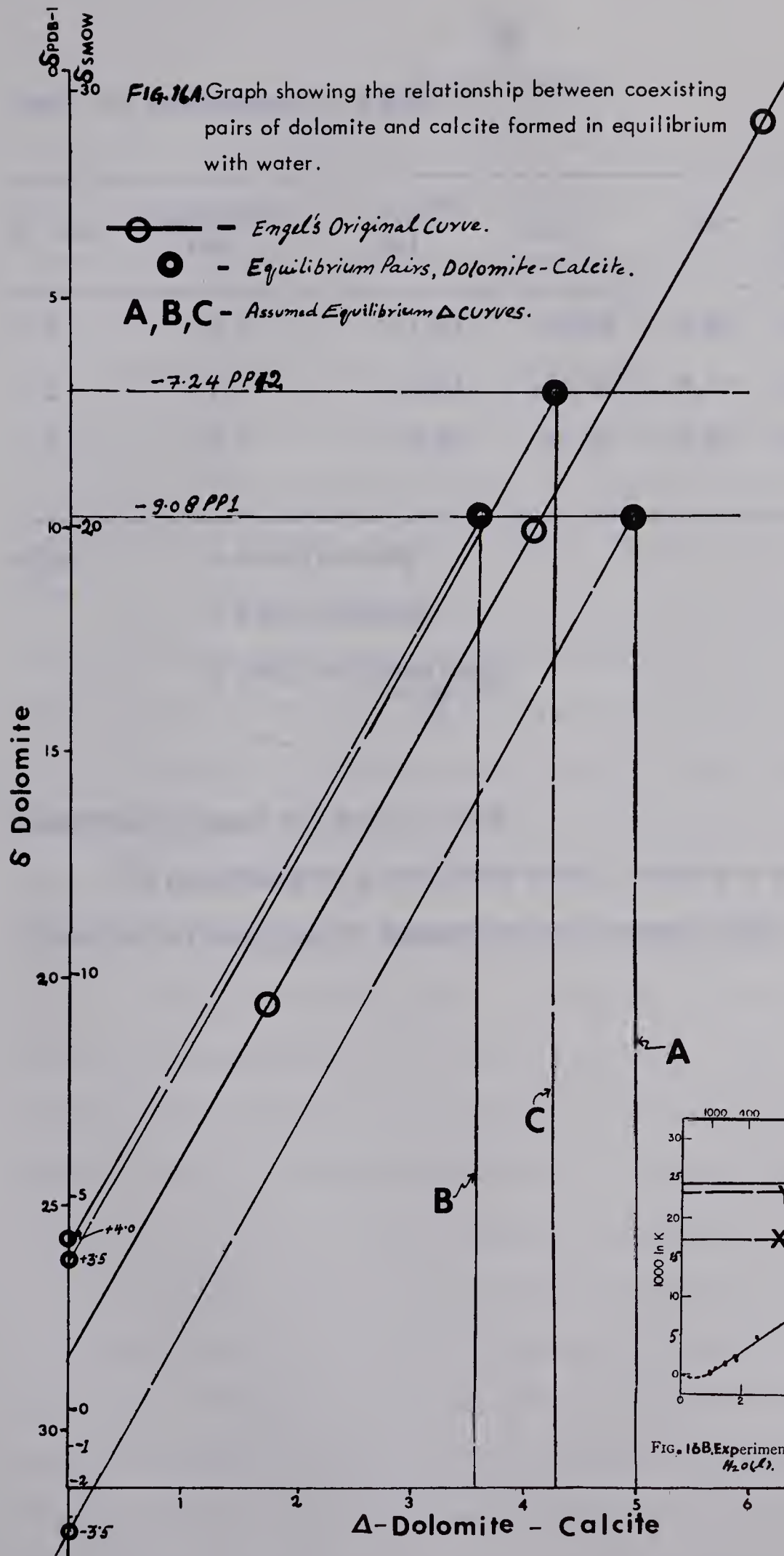


Table 16: Palaeotemperature data.

S. No.	Equilibrium Pair	O^{18} Dol.	Cal.	D-C	O^{18} water	Temp. °C
1.	X	-11.35	-14.05	-4.95	-3.5	100°C
2.	Y	-7.24	-11.39	-4.15	+3.5	50°C
3.	Z	-9.08	-12.67	-3.59	+4.0	48°C

Note -
 X = Pair PP1-PP8
 Y = Pair PP12-PP4
 Z = Pair PP1- $\frac{(PP2+PP8)}{2}$

were drawn by Degens and Epstein, 1964).

The paleotemperature evaluation makes it possible to conclude that Pine Point mineralization took place at temperatures not exceeding 100°C.

CONCLUSIONS

The foregoing discussion throughout this thesis brings out following salient points regarding the genetic problems of Pine Point mineralization.

1. The results of measuring the iron contents of sphalerite indicate that temperature of mineralization at Pine Point was less than 260°C. The FeS content in ZnS vary from 1 mole % to 15 mole % and this variation seems to have been caused by the changes in temperature and sulphur pressure. But recent experimental work of Barton and Toulmin (1966) invalidates the Fe-Zn-S system as a geothermometer below a temperature limit of 380°C. The system holds good in a temperature range of 380°C-850°C in an appropriate assemblage of pyrite-pyrrhotite-sphalerite. Though the Pine Point assemblage is pyrite-pyrrhotite-sphalerite type, the results obtained from FeS-ZnS ratios lie below the range where valid temperatures may be expected. In fact, the lower limit of 100°C obtained through this study for Pine Point mineralization is the maximum limit of mineralization as indicated by oxygen isotope geothermometry.
2. The study of magnesium contents in calcite lattice indicates a fairly low temperature for hydrothermal calcites grown in equilibrium with dolomite. The shift in calcite peaks was found to vary from zero to $0.01^\circ(2\theta_c - 2\theta_s)$. Since increase in angle $2\theta_c - 2\theta_s$ is temperature dependent a direct calculation of $MgCO_3$ in $CaCO_3$ lattice is possible. This study shows either no or extremely low amount of $MgCO_3$ in $CaCO_3$ which speaks for a low temperature of formation.
3. Textural studies suggest that open space filling was major method of ore deposition in Pine Point ore field, although some replacement of host rock has occurred on a minor scale. Paragenesis and mineral distribution suggests that uniform conditions prevailed throughout the course of mineralization but also suggests that earlier formed minerals were iron rich and later formed minerals zinc and lead rich. This interpretation indicates a slight change in the nature of mineralizing solutions. This change

might have been caused by introduction of certain minor elements from the rocks on its migration route.

4. Oxygen isotope geothermometry permits one to conclude that Pine Point mineralization took place over a temperature range of 100°C-50°C. The isotopic composition of carbon and oxygen for Pine Point carbonates seems fairly consistent.

The present study indicates that ore forming fluids in Pine Point ore field were rich in Pb-Zn-Fe ions. The transport of metals in solution may have occurred as metal chloride complexes through the available pore spaces and breccia zones. The metals finally precipitated in sulphur rich carbonate reservoirs. The sulphur was derived by direct reduction of sea water sulphates (Folinsbee *et al.*, 1966). Precipitation was probably caused by dilution of connate brines carrying base metal chloride complexes. This dilution of connate brines might have been caused by mingling with groundwater and wall rock reactions. Mineralization took place over a range of 100°C - 50°C. The work on oxygen isotope geothermometry is continuing in our laboratories and more precise data may be available in due course to further confirm the range of temperature of Pine Point mineralization.

EXPLANATION OF PLATES

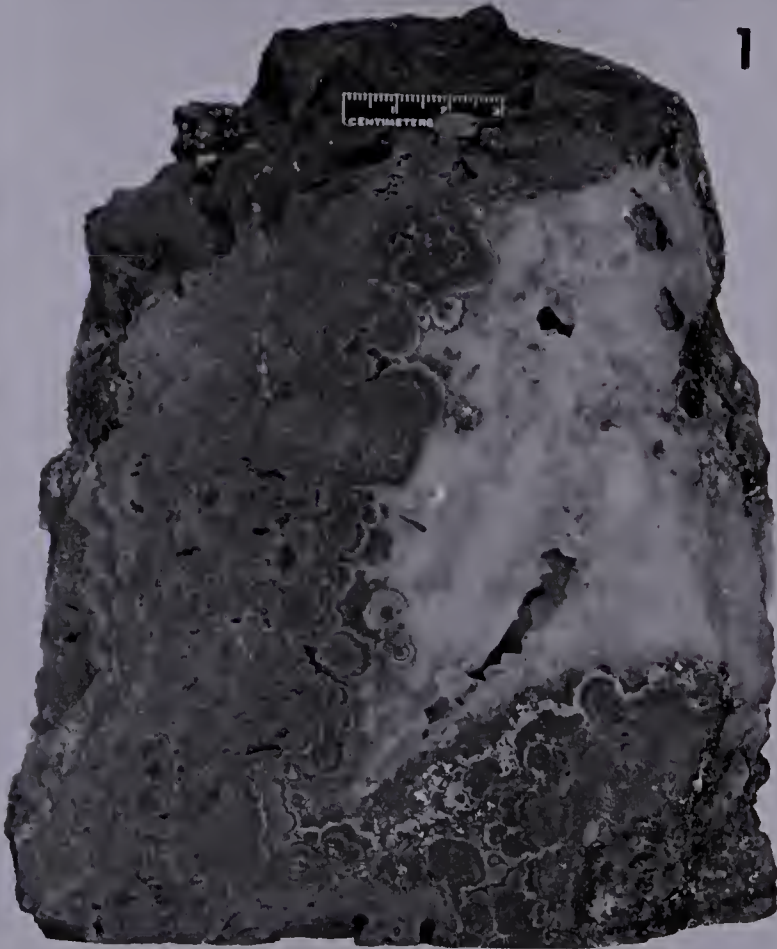
PLATE I

Figure

1. Hand specimen showing colloform texture. White crystallized dolomite in center surrounded by grey sphalerite.
2. & 3. Hand specimen showing two different views of the same sample. Colloform banding is more distinct.

PLATE-I

1



2



3

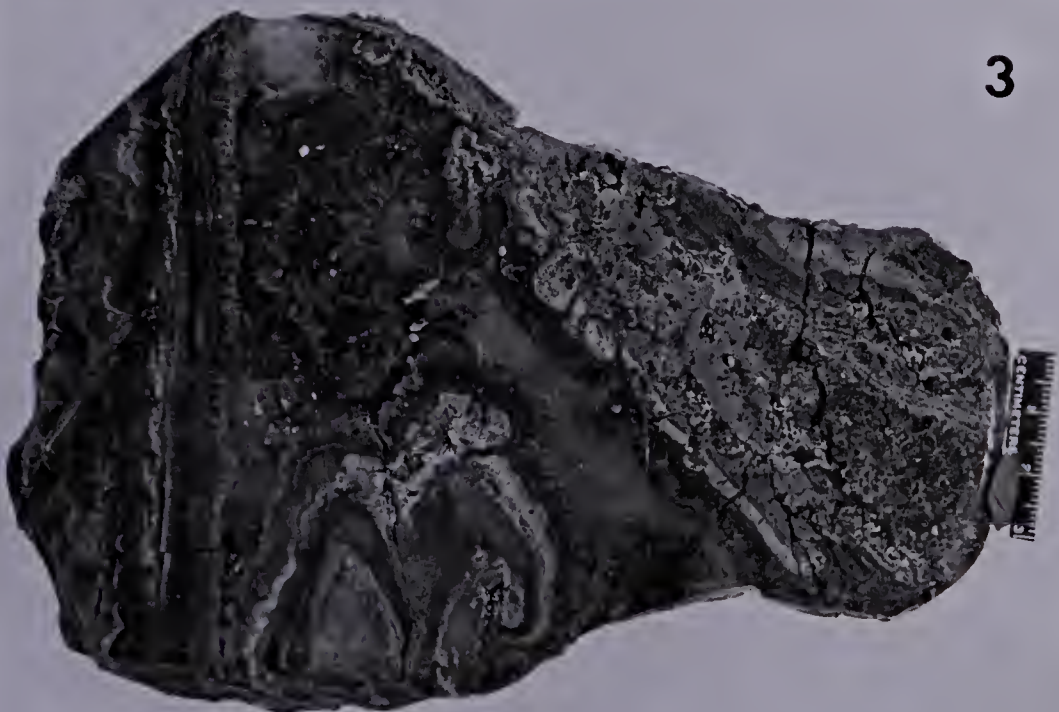


PLATE II

PHOTOMICROGRAPHS OF ORE SECTIONS

Figure

1. Colloform Texture - sphalerite bands show the colloform texture. Thin dark sphalerite bands arranged in alternate fashion with broad light sphalerite bands.
X260
Ref. No. P 29*, p. 46
2. Combined crustified and Ring Texture - Dark coloured sphalerite is in center followed by successive layers of light coloured sphalerite. Well developed galena crystals are sitting on the top of light sphalerite band.
X25
Ref. No. P 29+, p. 46
3. Rosette Texture - Rounded pollen like sphalerite aggregate represents rosette texture. Dark sphalerite is in the middle and is surrounded by the light sphalerite, white mass is dolomite.
X25
Ref. No. P 29+, p. 46
4. Atoll or Core Texture - Galena cubes (black in picture) are surrounded by the alternate bands of light and dark sphalerite. Galena cubes served as core.
X25
Ref. No. P 29+, 46
5. Replacement of dolomite (white-grey) along the rhombohedral cleavage planes by sphalerite (grey).
X260
Ref. No. N-42-C/1*, p. 47
6. Cockade-Crustification Texture - Sphalerite (light grey) crystals pointing towards the center of the cavity. They are arranged perpendicular to the wall of the cavity. The cavity is filled with dolomite (white) and also presence of dark sphalerite (greyish-black) could be noted.
X260
Ref.No. N-42-C/1*, p. 47
7. Comb Texture - Sphalerite crystals (white-grey) present on the wall of cavity (dark grey sphalerite) showing comb texture.
X260
Ref.No. N-42-C/1*, p. 47
8. Dendritic Texture - Galena needles (black) are arranged in a dendritic fashion and are embedded in dark coloured sphalerite.
X25
Ref. No. N-42-C/1+, p. 47

* Indicates polished ore section
+ Indicates thin ore section

PLATE - II

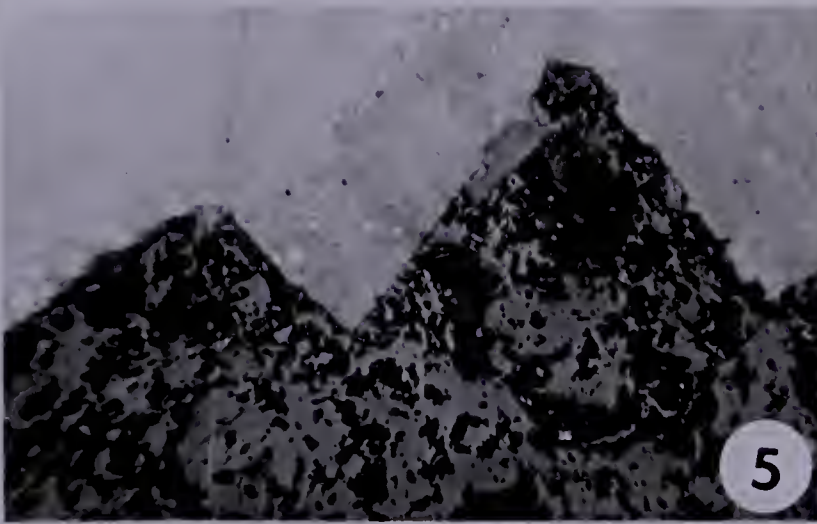
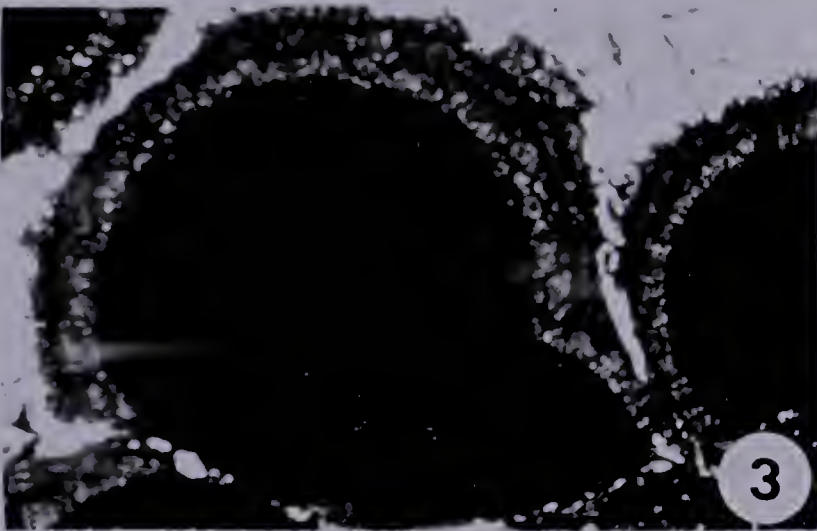
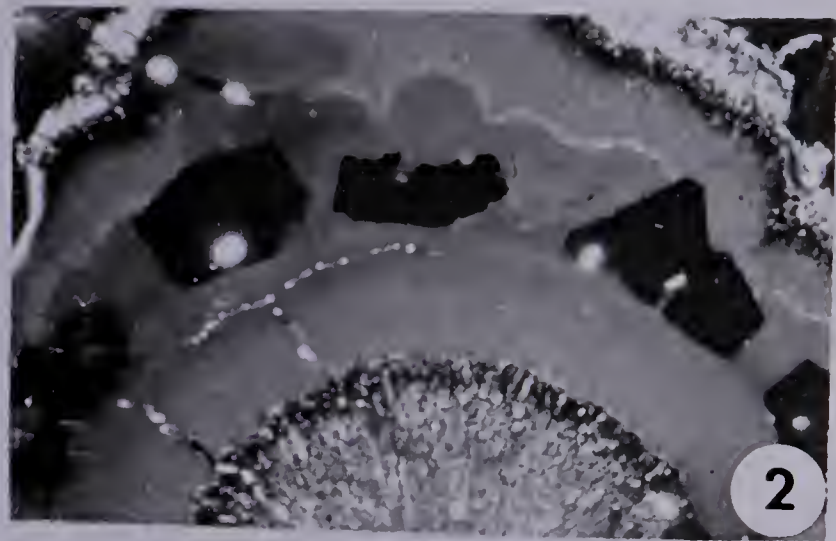
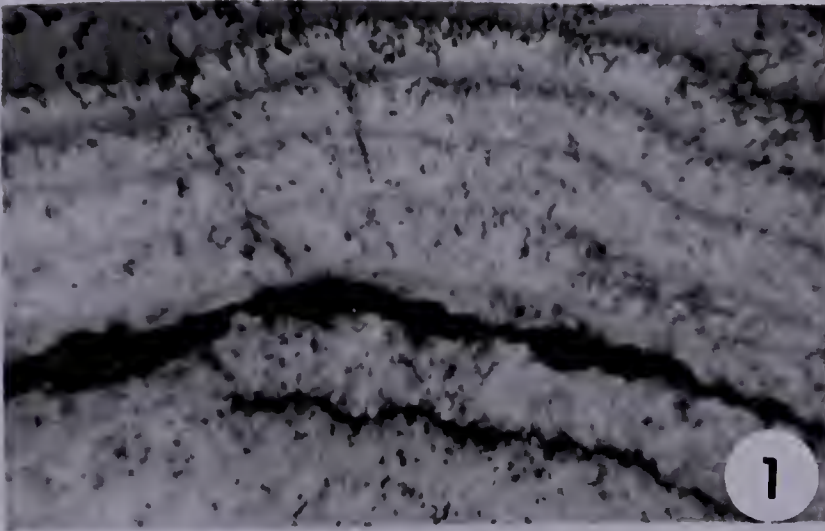


PLATE III

PHOTOMICROGRAPHS OF ORE SECTIONS

Figure

1. Cavity Filling Texture - Galena (black) seems filling the cavity left after the precipitation of sphalerite (grey and greyish-white).
X25
Ref. No. N-42-c/1+, p. 47
2. Sharp contact between sphalerite (grey) and pyrite-marcasite mass (white) is well represented. Numerous dolomite inclusions (black) are present in pyrite-marcasite mass.
X260
Ref. No. N-42-C/3*, p. 48
3. Arrangement of pyrite (white), sphalerite (grey) and calcite could be seen. Calcite crystal shows lamellar twinning.
X25
Ref. No. N-42-C/3+, p. 48
4. Fine grained dolomite shows cleavage and fracture planes.
X25
Ref. No. N-42-C/3+, p. 48
5. Mutual Boundary Texture - Galena (light grey), sphalerite (medium grey) and dolomite (grey) crystals show their mutual boundaries.
X260
Ref. No. N-42-C/5*, p. 49
6. Core Texture - Euhedral galena crystal (white-grey) is enveloped by the sphalerite rim.
X260
Ref. No. N-42-C/5*, p. 49
7. Spheroidal or Pellet Texture - Dark sphalerite (in the center of spheroid) is enveloped by light sphalerite.
X260
Ref. No. N-42-C/5*, p. 49
8. Zonal Texture - Sphalerite crystal shows zoning phenomenon.
X260
Ref. No. N-42-C/5*, p. 49

* Indicates polished ore section

+ Indicates thin ore section

PLATE-III

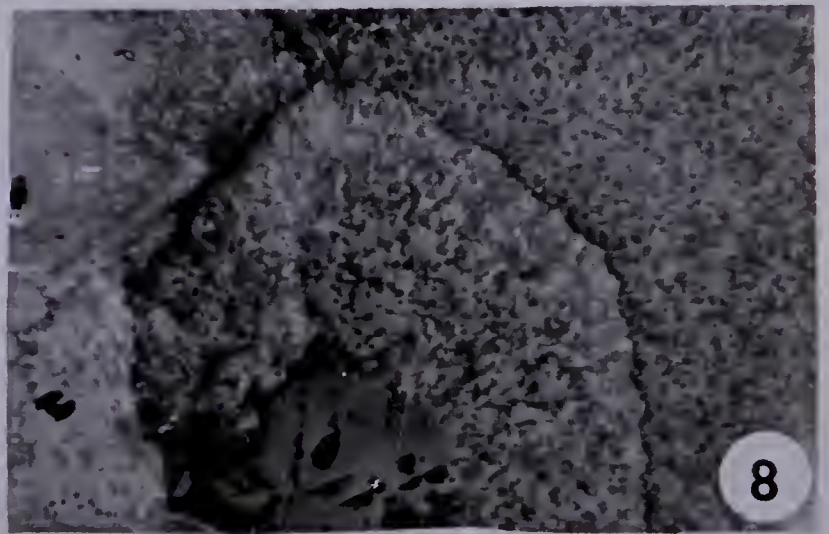
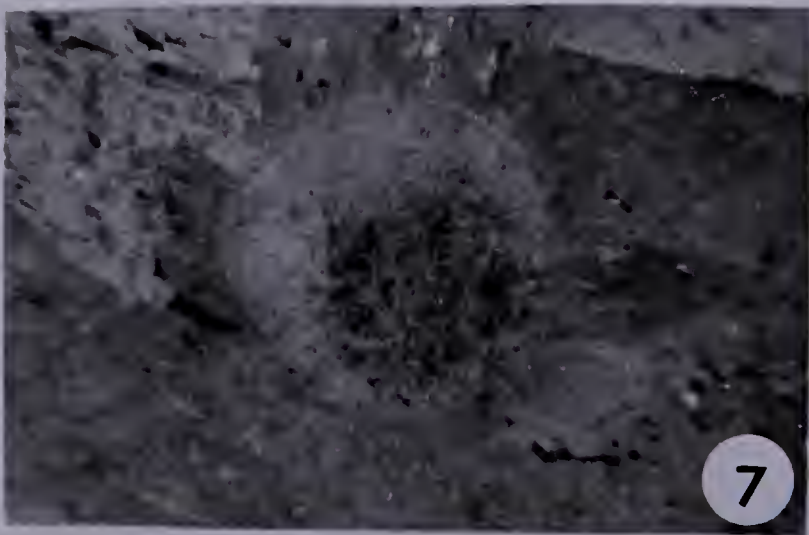
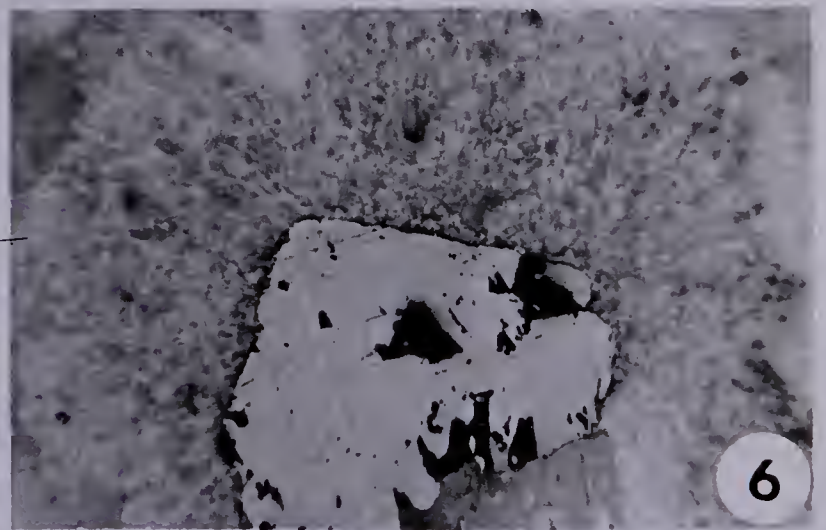
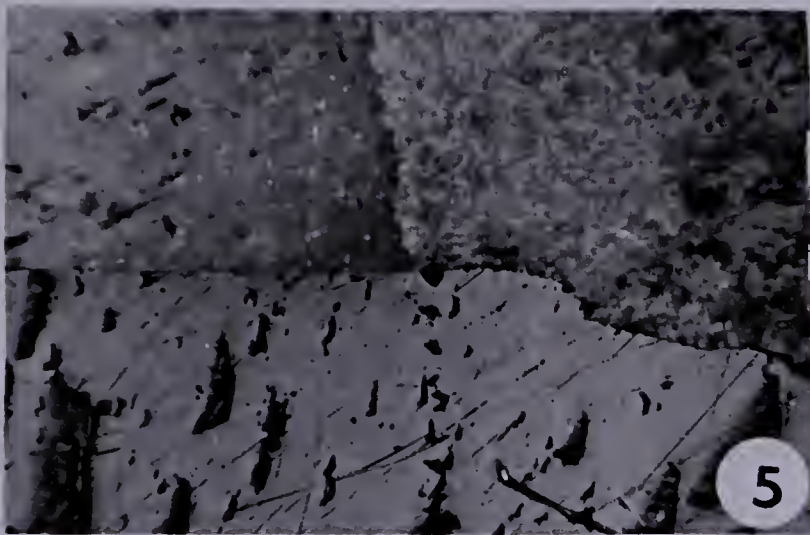
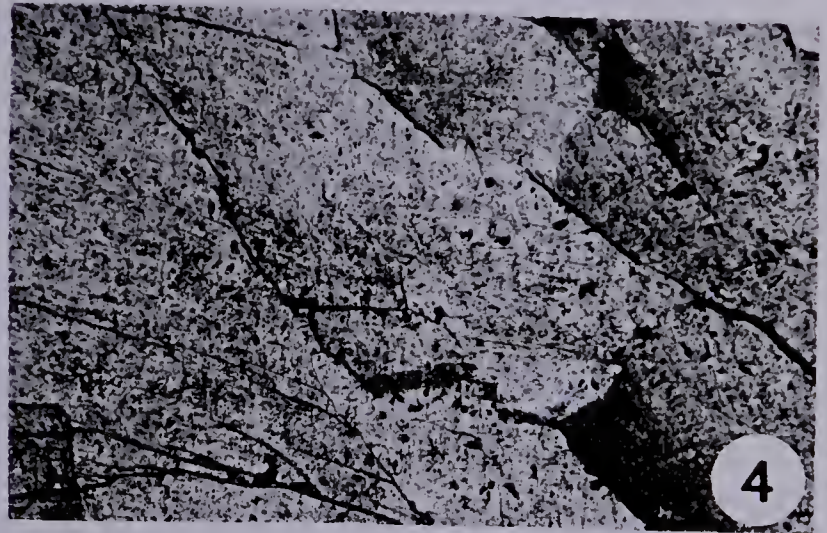
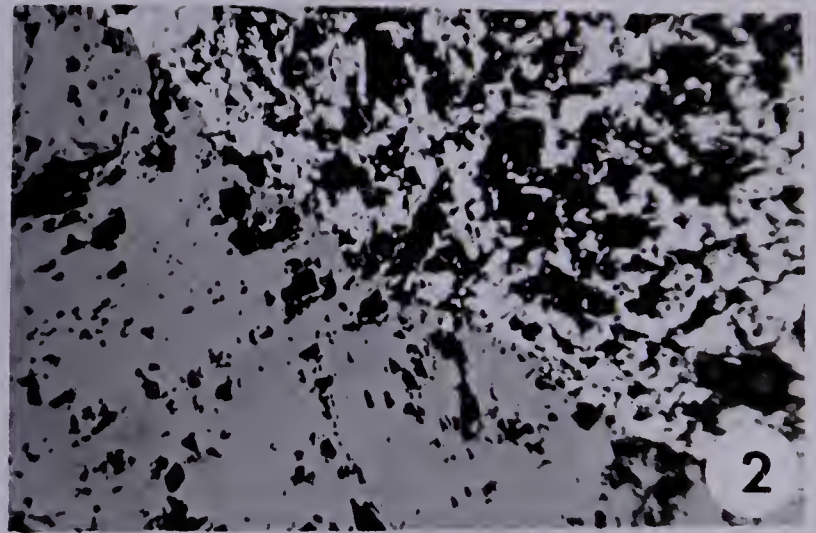
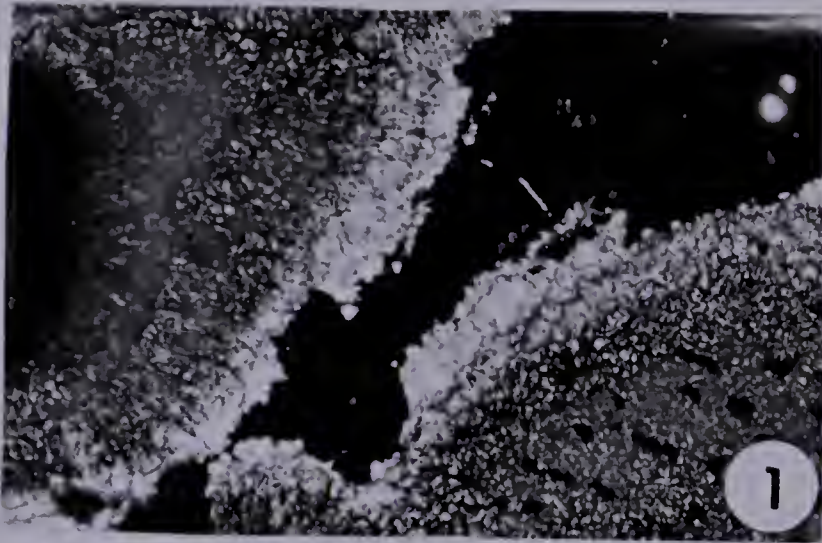


PLATE IV

PHOTOMICROGRAPHS OF ORE SECTIONS

Figure

1. Metacolloidal or Crackled Texture - Dark sphalerite in center is surrounded by light sphalerite. Several cracks developed and seen intersecting each other. X162
Ref.No. N-42-C/5+, p. 49
2. Replacement of dolomite (grey) by galena (white) along the cleavage plane. X260
Ref.No. N-42-C-3*, p. 50
3. Replacement of sphalerite (light grey) by galena (white). X260
Ref.No. N-42-C-3*, p.50
4. Colloform Texture - Excellent representation of colloform texture by alternating bands of light and dark coloured sphalerite. Ref.No. N-42-C-3+, p. 50
5. Dendritic texture - Galena (black) shows dendritic texture. Groundmass is sphalerite (grey). X25
Ref.No. N-42-C-3+, p. 50
6. Box Work Texture - Sphalerite mass is traversed by several intersecting septa which gave rise to polygonal boxes. X25
Ref.No. N-42-C-3+, p. 50
7. Hypidiomorphic Texture - Euhedral - subhedral marcasite crystals (greyish-white) are embedded in sphalerite mass (dark grey). X260
Ref.No. O-42-C-1(C)*, p.50
8. Spheroidal or Pellet Texture - Small pellets of sphalerite (black) are embedded in dolomite crystal (greyish-white). X260
Ref. No. O-42-C-1(C)*, p.50.

* Indicates polished ore section

+ Indicates thin ore section

PLATE-IV

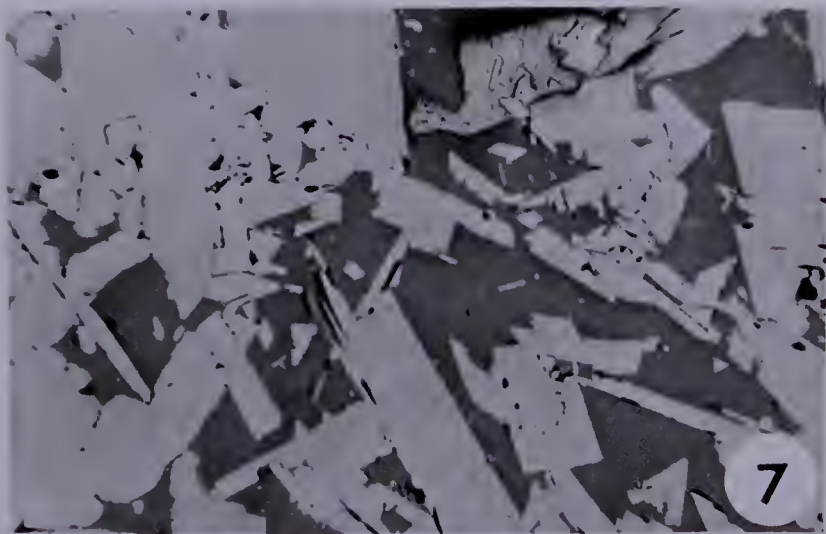
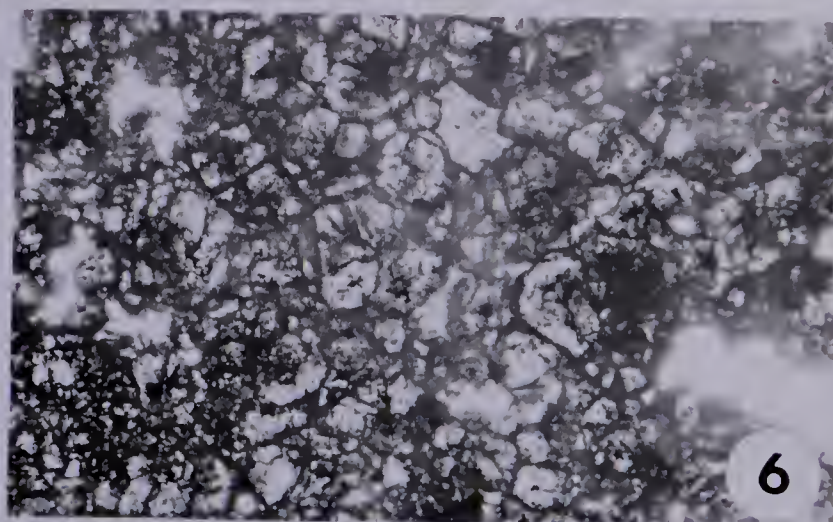
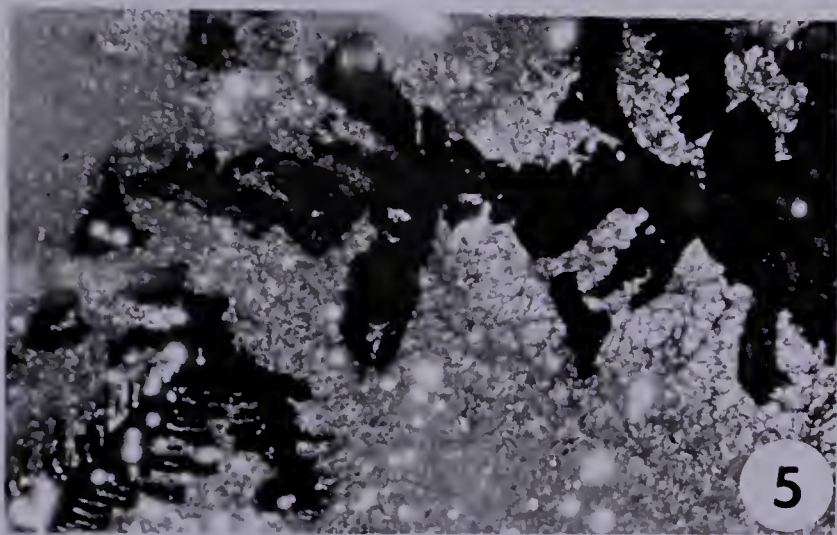
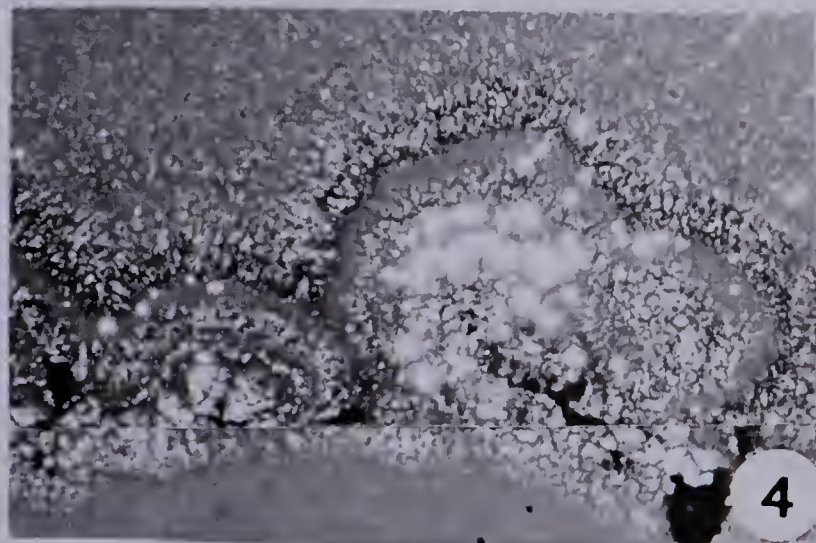
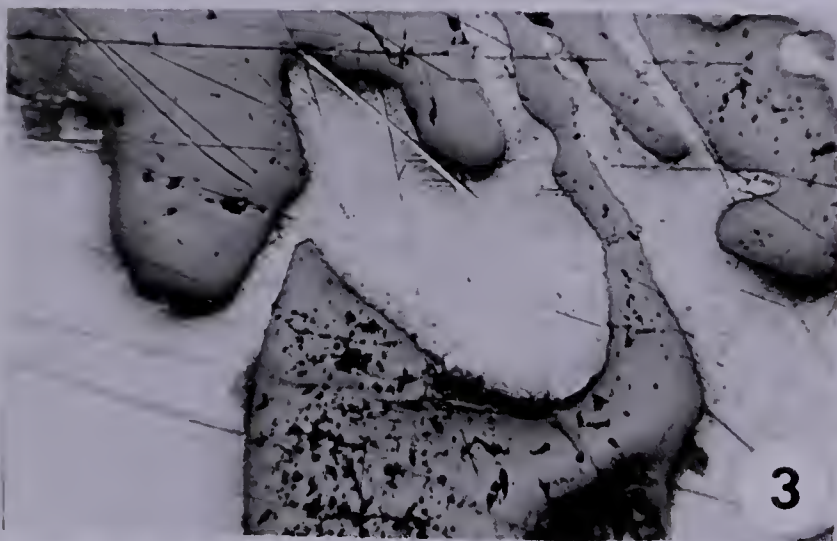
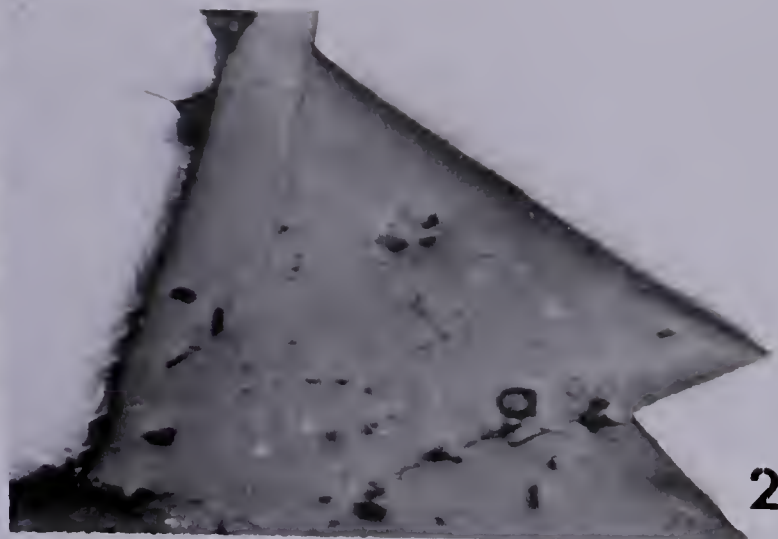
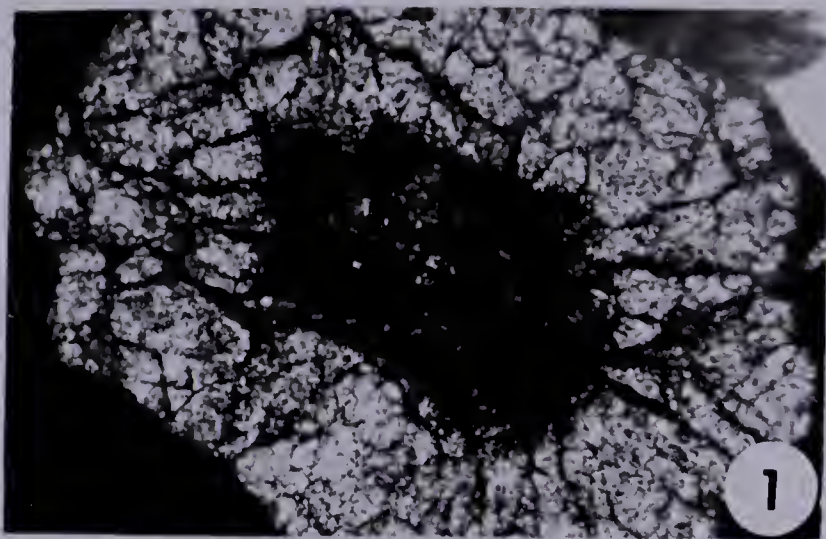


PLATE V

PHOTOMICROGRAPHS OF ORE SECTIONS

Figure		Ref. No. Page
1.	<u>Zonal Texture</u> - Dolomite crystal shows zoning. X260	PP-A*, 52
2.	<u>Lamellar/Triangular Texture</u> - spindle shaped marcasite laths (white) are embedded in dolomite (grey) matrix. X260	PP-A*, 52
3.	<u>Lamellar/Triangular Texture</u> - Pyrrhotite laths (grey) are embedded in dolomite matrix (white-grey). X260	PP-A*, 52
4.	Contact of pyrite (white) and sphalerite (grey) showing small stringers of sphalerite intruding in the pyrite. X260	PRM-1*, 53
5.	Several globules of sphalerite (grey) are enclosed by galena mass (white) showing that sphalerite was earlier to precipitate and being replaced by galena. X260	PRM-1*, 53
6.	<u>Colloform Texture</u> - Colloform bands of sphalerite (grey and light grey) are seen in contact with pyrite (white). X260	PRM-1*, 53
7.	Shredded Texture - Irregular grains of pyrite (white) are embedded in sphalerite mass (grey).	PRM-1*, 53
8.	<u>Mutual Boundary Texture</u> - Sphalerite (dark grey), galena (light grey) and pyrite (white-grey) are seen in close contact exhibiting mutual relationships. X260	PRM-2A*, 54

PLATE-V

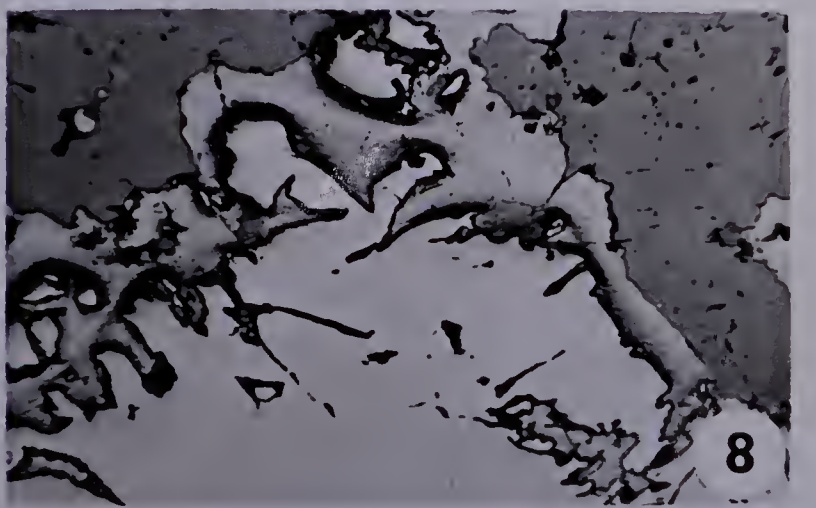
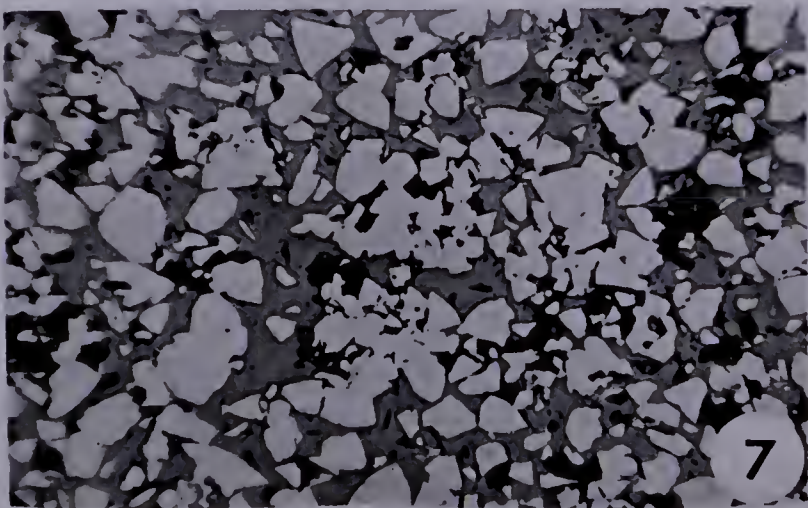
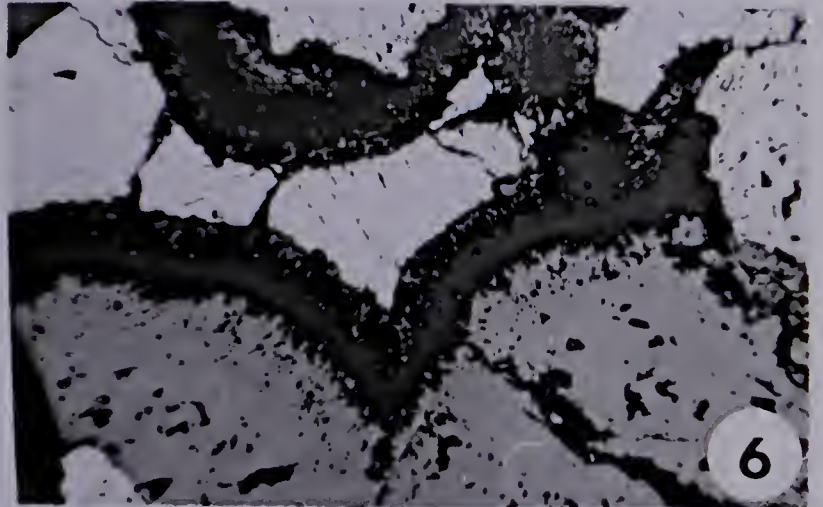
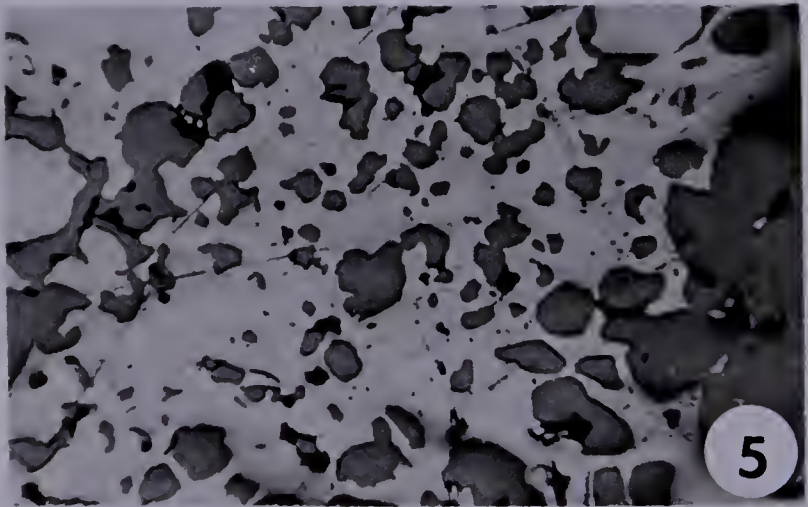
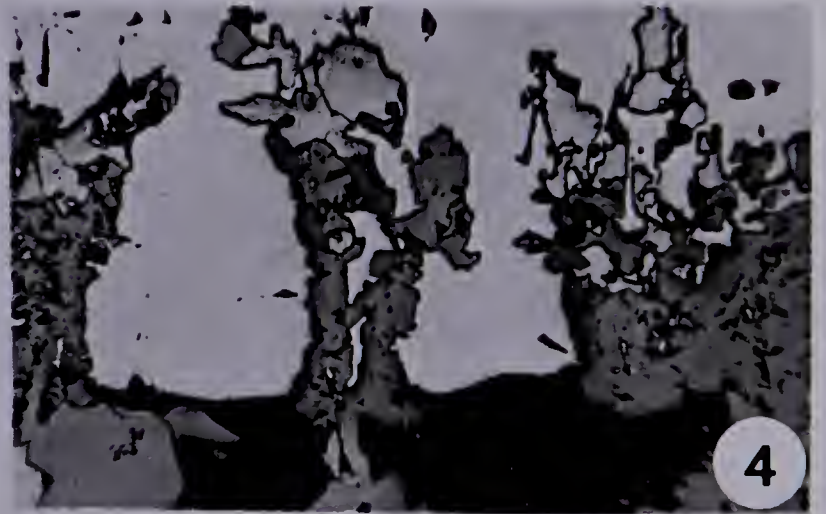
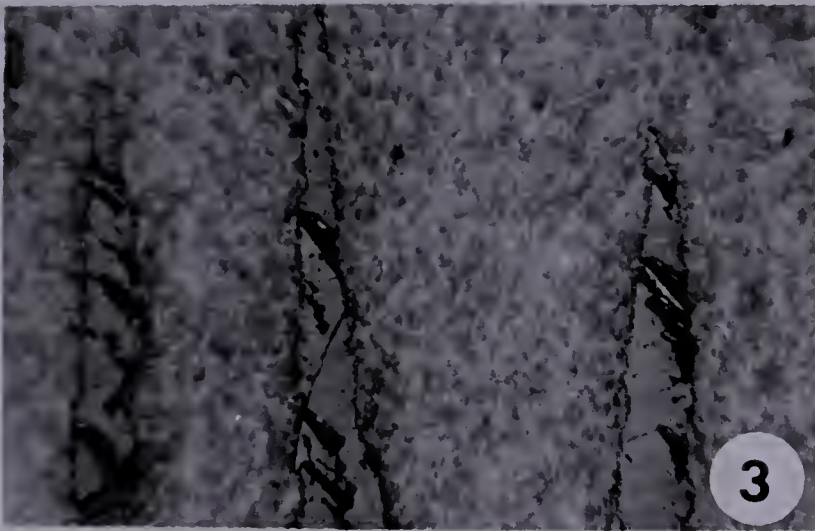


PLATE VI

MICROPHOTOGRAPHS OF ORE SECTIONS

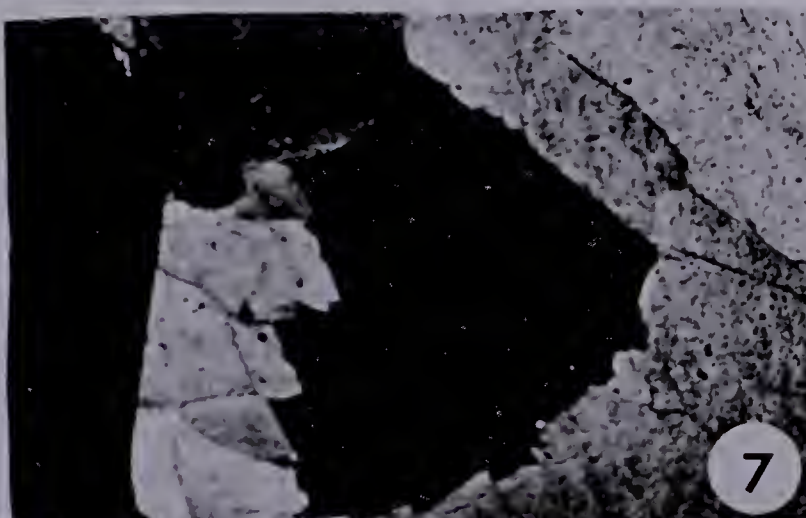
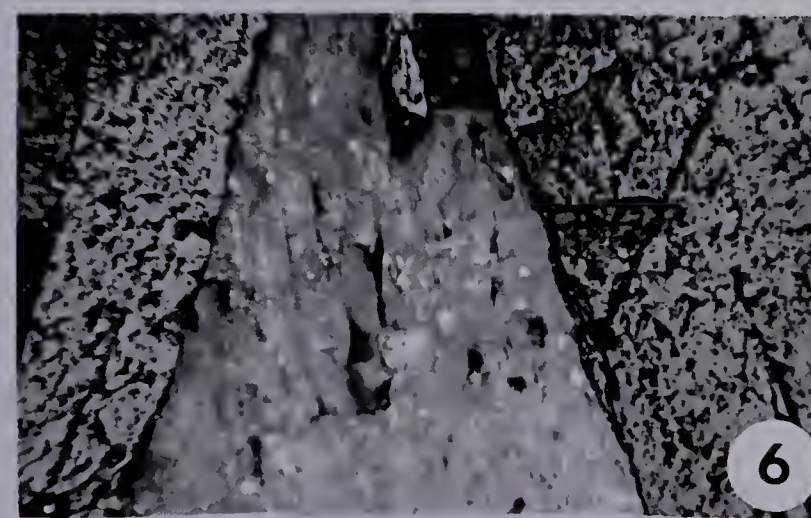
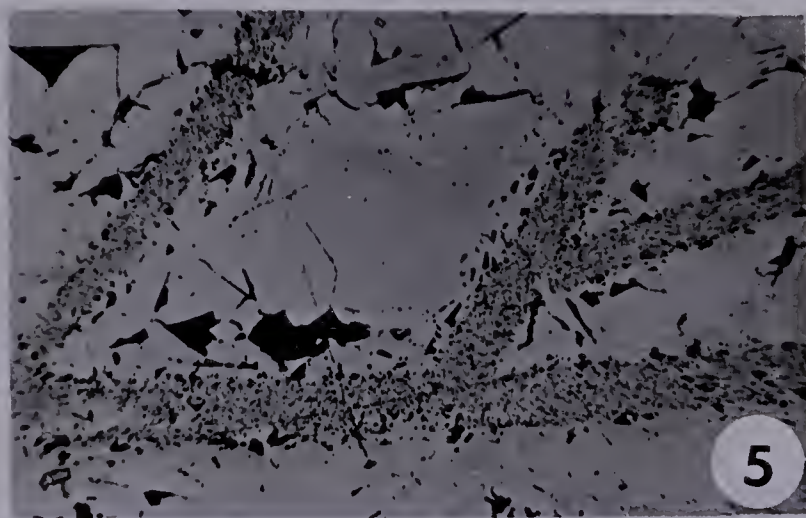
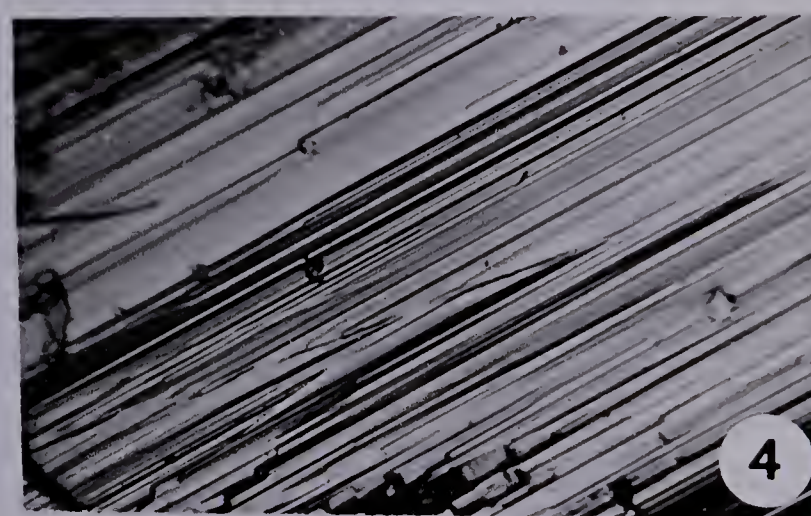
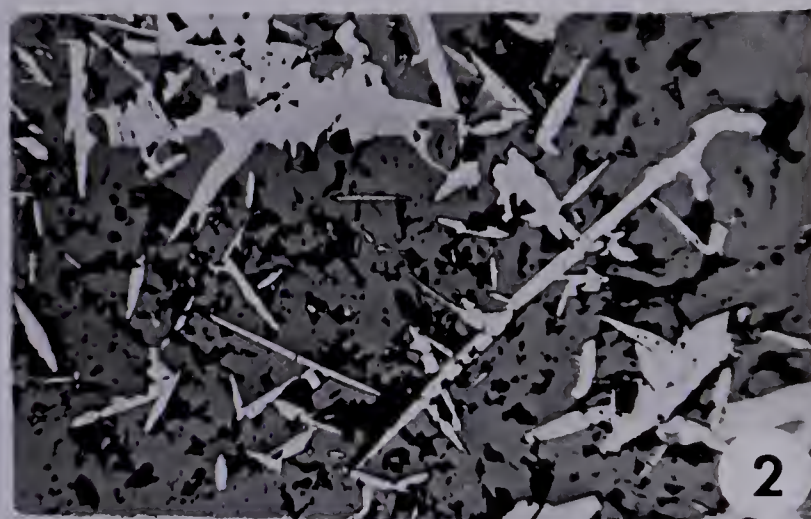
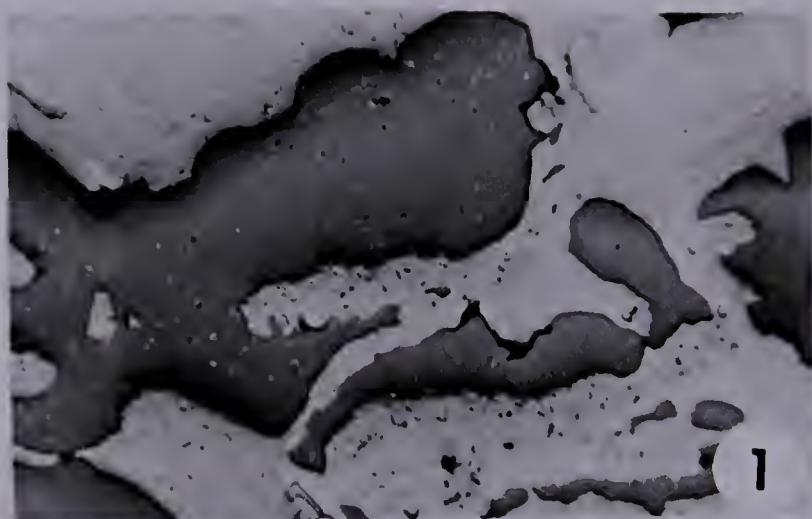
Figure

1. Sphalerite (grey) is being replaced by the galena (white).
Sphalerite blebs are embedded in galena mass. X260
Ref.No. PRM-2A*, p. 54
2. Needle Shaped Texture - Needle like marcasite crystals
(white) are embedded in the pyrite-sphalerite matrix
(grey). X260
Ref.No. PRM-2A*, p.55
3. Rim Texture - A grain of dolomite (black) is surrounded
by the pyrite (greyish-white) and successively followed
by marcasite (white). X260
Ref.No. PRM-2B*, p.55
4. Dolomite crystal shows twinning. X260
Ref.No. PRM-2B*, p. 55
5. Lamellar Texture - Pyrite laths (dark grey) are embedded
in the marcasite mass (light grey). Dolomite inclusions
are seen (black). X260
Ref.No. PRM-2B*, p. 55
6. Pyrite laths (grey) are enclosing dolomite crystals
(white-grey). X260
Ref.No. PRM-2B*, p. 55
7. Comb Texture - Well developed sphalerite crystals (white)
are present in the wall of cavity. Dolomite (black) is
in the center. X25
Ref.No. PRM-2B+, p. 55
8. Porphyroblastic Texture - Pyrite cubes (white) are embedded
in dolomite mass (dark grey). X260
Ref.No. PRM-3*, p. 56

* Indicates polished ore section

+ Indicates thin ore section

PLATE - VI



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APPENDIX - 1

SAMPLE COLLECTION-

The samples used in this study were collected from the Pine Point and Pyramid pits located in Pine Point ore field, N.W.T. The samples were collected in such a manner as to get a fairly accurate cross section of the ore body. The plan of collection and location of each sample is given in figures A₁ and A₂. Many samples were collected right on top of the orebody and a few from the ramp.

LOCALITY INDEX-

Samples were collected from Pine Point mine with a few exceptions. General index is given below but for detail, the description in Table 18, in Appendix III may be referred to.

General Index

S.No.	Locality	Remarks
1.	Pine Point Ore Field	Ore samples used in this study were collected from the Pine Point Pits - P29, N-42 and O-42.
	Pine Point Ore Field	Four samples were collected from the Pyramid pits and at the top of the orebody.
2.	Windy Point	One sample was collected from the Windy Point area.

APPENDIX - II

DETERMINATION OF IRON CONTENTS IN SPHALERITESSAMPLE PREPARATION AND DETERMINATION TECHNIQUE:-

Major ore contents at Pine Point are lead and zinc. Among sulfides sphalerite is widespread mineral. Sphalerite samples studied and analysed in this study were collected from the Pine Point pits. A precise account is given in Table 17. All samples were collected either from the top of the orebody or near the orebody (see Figs. A₁ and A₂).

In the laboratory, the sulfide ores were separated in such a way that no visible contamination was observed. The sphalerite bands were broken with the help of a small hammer and, then after all the sphalerite grains were handpicked under a binocular microscope. Same process was repeated for all dark and light sphalerite samples. An attempt was made to remove all possible contaminants from the samples. However, galena which is finely intergrown with the sphalerite in many ore samples could not be removed completely. Only trace of galena may therefore be expected in sphalerite samples. The hand picked grains of light and dark coloured sphalerite were ground separately in an agate mortar to their powder form. The sample, thus obtained were kept in small bottles for the chemical and X-ray studies.

All dark and light coloured sphalerites were chemically analysed by hexachloroferrate method for their mole per cent FeS determination.

All samples prepared for X-ray fluorescence analysis were briquetted in an Applied Research Laboratories Inc. Briquetting machine Type 4451, for 60 seconds at 30,000 p.s.i. Each sample was backed and rimmed with cellulose powder for strength. The diameter of the exposed sample was approximately 1/4 inch. A Quantitative analysis for the minor elements determination in sphalerite was done and sphalerite peak with maximum intensity was assumed to have 15.80 mole % FeS (Maximum mole % FeS obtained by chemical method). The calculations were made

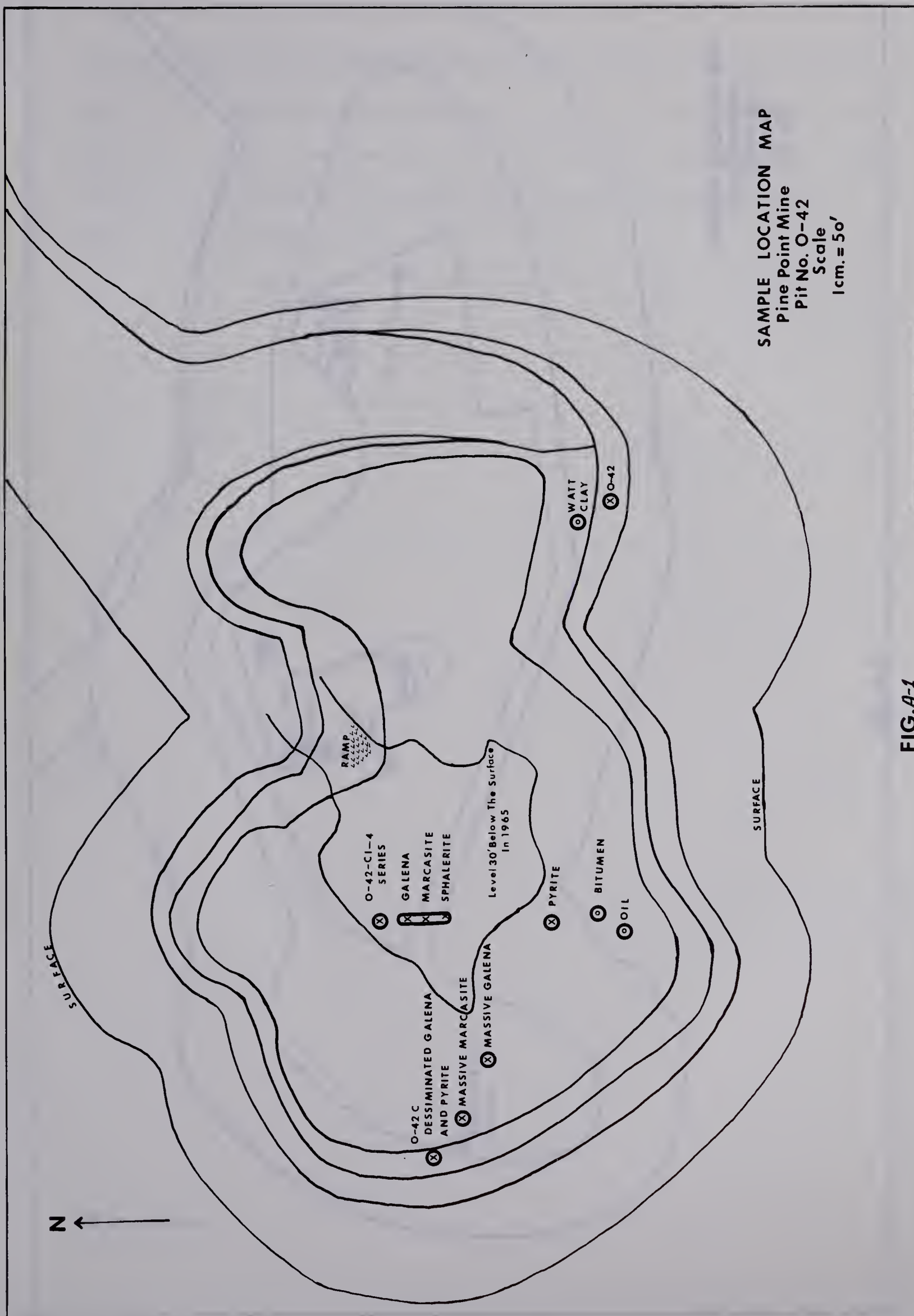
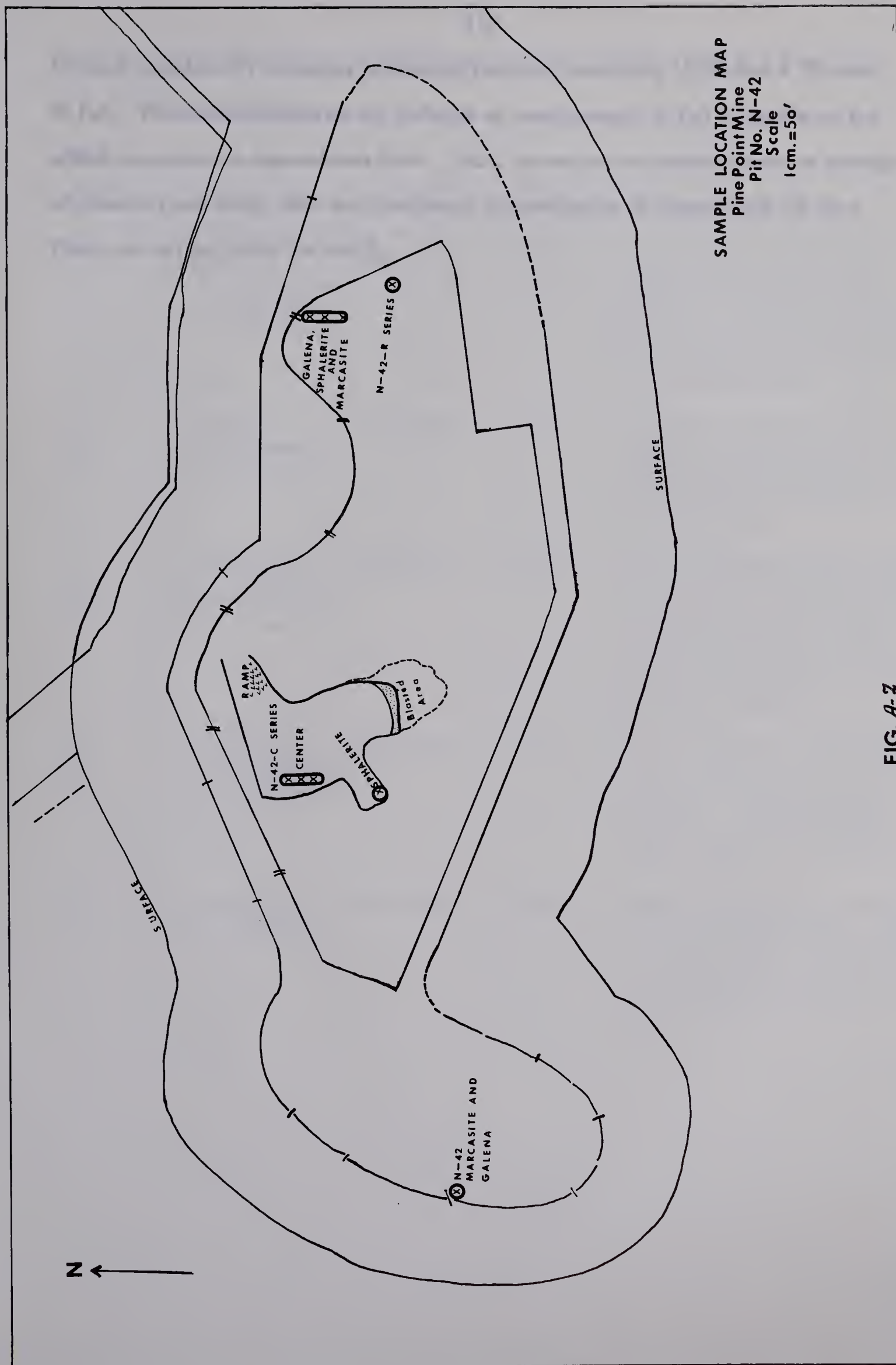


FIG. A-1



for each sample with reference to assumed standard containing 15.80 and 4.90 mole % FeS. These calculations do not indicate an exact amount of FeS in sphalerite but afford to explain an approximate limit. Thus, to reduce the probable error an average of chemical and X-ray data was considered for evaluation of temperatures for Pine Point sphalerites (Table 3A and B).

Table 17. Description of the sulfide samples used for Chemical Analysis, Pine Point
Orefield, N.W.T.

S. No.	Sample No.	Locality	Pit No.	Sample Description
#	P29	Pine Point	P29	
1.	Dk. sphalerite			Massive ore containing sphalerite and galena with little dolomite. Colloform banding shows arrangement of light and dark coloured sphalerite bands in the hand specimen.
2.	Lt. sphalerite			
#	N-42-C-1	Pine Point	N-42	
3.	Dk. sphalerite			Similar to above but sphalerite and galena crystals are segregated. Dk. sphalerite band is in center surrounded by Lt. sphalerite band.
4.	Lt. sphalerite			
#	N-42-C-3	Pine Point	N-42	
5.	Dk. sphalerite			Several rhythmic bands of light and dark sphalerite are seen in hand specimen. Sphalerite is very fine grained but galena is well crystallized and shows well developed cubes. A little marcasite is present.
6.	Lt. sphalerite			
#	N-42-C-4	Pine Point	N-42	
7.	Dk. sphalerite			Dark coloured crystalline sphalerite. Bands of dark and light sphalerite enclosing fine grained marcasite. Little dolomite is present. No trace of galena in this sample.
8.	Lt. sphalerite			
#	O-42-C-1	Pine Point	O-42	
9.	Lt. sphalerite			Assemblage of galena, sphalerite and pyrite is noted. Ore is of massive form. Light coloured bands are seen but dark coloured bands are scarcely seen.

APPENDIX - III

DETERMINATION OF MINOR ELEMENTS IN SULFIDESSAMPLE PREPARATION AND DETERMINATION TECHNIQUE

The sphalerite, galena and marcasite samples were prepared according to procedure already given in Appendix II. The technique for making X-ray targets was also the same as described in Appendix II. In all, twenty-seven samples were analysed for their minor elements. Of these, 9 were dark and light coloured sphalerites, 3 galenas, 2 marcasites and 13 whole ore samples. These thirteen polished ore sections were also used for microscopic studies. A brief description of each sample used in this study is given in Table 18.

The following general set-up was maintained throughout the course of X-RF experiments.

X-Ray Unit	Norelco-X-ray Fluorescence Unit type 12215/0
Radiation source	MO Target Tube
Radiation Conditions	50 K.V. 40 M.A.
Analysing Crystal	Lithium Fluoride Crystal
X-Ray Path	Air
Counter Used	Scintillation Counter
Detector voltage	Range 850-900 K.V.
Seal Factor	Variable
Operation	Continuous

Table 18. Description of sulfide samples used in determination of minor elements by X-ray Fluorescence method.

S.No.	Sample No.	Locality	Pit No.	Description	Remarks
1.	P 29	Pine Point	P 29	Ore sample P 29 contains galena and marcasite in addition to sphalerite. The dark and light sphalerite bands are sharp.	Dark sphalerite was separated for x-ray use.
2.	P 29 Lt. sphalerite	"	"	Same as above	Lt. sphalerite was separated for x-ray use.
3.	N-42-C-1 Dk. sphalerite	"	N-42	Ore sample contains galena, marcasite and sphalerite. Dark sphalerite is in center and enveloped by light sphalerite.	Dark sphalerite was separated for x-ray use.
4.	N-42-C-1 Lt. sphalerite	"	"	Same as above	Lt. sphalerite was separated for x-ray use.
5.	N-42-C-3	"	"	Ore sample contains sphalerite, marcasite, galena and dolomite. Rhythmic bands of light and dark sphalerite are conspicuous.	Dark sphalerite was separated for x-ray use.
6.	N-42-C-3 Lt. sphalerite	"	"	Same as above	Lt. sphalerite was separated for x-ray use.
7.	N-42-C-4 Dk. sphalerite	"	"	Ore sample contains dark coloured crystalline sphalerite and marcasite. Dark and light sphalerite bands present in alternate fashion.	Dk. sphalerite was separated for x-ray use.
8.	N-42-C-4 Lt. sphalerite	"	"	Same as above	Lt. sphalerite was separated for x-ray use.
9.	O-42-C-1 Lt. sphalerite	"	O-42	Ore sample contains galena, sphalerite and pyrite. Light sphalerite bands alternate with very thin dark sphalerite bands.	Lt. sphalerite was separated for x-ray use.
10.	P 29	"	P 29	Description of ore sample	Separated

Table 18...continued
Galena

				is same as for P 29 sphalerite ore sample. The galena was separated from the same sample.	galena was used for x-ray analysis.
11.	N-42-C-1 Galena	Pine Point	N-42	Description is same as given in case of N-42-C-1 ore sample containing sphalerite.	"
12.	N-42-C-3 Galena	"	"	Description is same as given in case of N-42-C-3 ore sample containing sphalerite.	"
13.	O-42-C-1	"	O-42	Description is same as given in case of O-42-C-1 ore sample containing sphalerite.	Marcasite was separated for x-ray analysis.
14.	N-42-C-4	"	N-42	Description is same as given in case of N-42-C-4 ore sample containing sphalerite.	"
15.	N-42-C-1	"	"	Ore sample contains sphalerite galena and dolomite. Clear crustification and small scale veining is seen.	Polished ore section was used for x-ray analysis.
16.	N-42-C-2	"	"	Ore sample contains light and medium brown sphalerite with dolomite. Sphalerite shows rhythmic bands probably filling the cavities in dolomite.	Polished ore section was used for x-ray analysis.
17.	N-42-C-3	"	"	Ore sample contains sphalerite, pyrite and dolomite. Sharp sphalerite contact with that of pyrite is distinct.	"
18.	N-42-C-4	"	"	Ore sample contains sphalerite pyrite and marcasite. Dolomite is present as gangue mineral.	"
19.	N-42-C-5	"	"	Little galena cubes and light sphaleroids are embedded in dolomite mass. Little pyrite is seen in contact with dolomite.	"
20.	PP-A	"	Core sample 55' depth	Presence of pyrrhotite, pyrite, and marcasite is noted in this ore sample. Dolomite is present as gangue mineral.	Polished ore section was used for x-ray analysis.
21.	PP-B	"	"	Same as above	"

Table 18...continued

22.	PP-M	Pine Point	not known	Ore sample contains dark sphalerite, galena and dolomite. Sphalerite forms small vein.	"
23.	WP	Windy Point -		Ore sample contains sphalerite and dolomite. Sphalerite is dark brown in colour. Well developed galena crystals are embedded in dolomite-sphalerite mass.	"
24.	PRM-1	Pine Point	Pyramid Pit	Ore sample contains pyrite, marcasite and sphalerite. A little galena is seen associated with the ore.	"
25.	PRM-2A	"	"	Same as above but shows sharp contact of dark sphalerite and pyrite.	"
26.	PRM-2B	"	"	Ore sample contains only marcasite and intergrown pyrite. Little dolomite with traces of galena and sphalerite.	"
27.	PRM-3	"	"	Ore sample contains pyrite, marcasite along with little galena and sphalerite.	"

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